

# Density functional approach to the many-body problem: key concepts and exact functionals

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## Abstract

We give an overview of the fundamental concepts of density functional theory. We give a careful discussion of the several density functionals and their differentiability properties. We show that for nondegenerate ground states we can calculate the necessary functional derivatives by means of linear response theory, but that there are some differentiability problems for degenerate ground states. These problems can be overcome by extending the domains of the functionals. We further show that for every interacting  $v$ -representable density we can find a noninteracting  $v$ -representable density arbitrarily close and show that this is sufficient to set up a Kohn-Sham scheme. We finally describe two systematic approaches for the construction of density functionals.

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## 1. Introduction

In this paper we give an overview of the foundations of density functional theory for stationary systems. In the discussion we try to be as precise as possible and we therefore carefully discuss several exact density functionals and the domains of densities on which they are defined. At the heart of almost any application of density functional theory lie the Kohn-Sham equations. These equations describe a noninteracting system that is required to produce the ground state density of an interacting system. Therefore any discussion of the validity of these equations has to focus on how well we can approximate a density of an interacting system with that of a noninteracting system. Closely related to this question is whether or not the exact functionals that we defined have functional derivatives. This is because the various potentials, such as the Kohn-Sham potential, in density functional theory appear as functional derivatives of the energy with respect to the density. The investigation of the existence of functional derivatives will form a central theme of this review.

A large part of this work will follow the proofs of the fundamental papers by Lieb [1] and Englisch and Englisch [2, 3]. In this paper we try to make these two important works more accessible by providing some background on the mathematics involved. We further show, from a more physical viewpoint, how to calculate functional derivatives by response theory and show that for nondegenerate ground states the static density response function is invertible. We also show that for every interacting  $v$ -representable density there is a noninteracting  $v$ -representable density arbitrarily close to it and that this is sufficient to set up a Kohn-Sham scheme. We finally discuss two systematic approaches for the construction of the exchange-correlation functional and provide an outlook and conclusions.

## 2. Definition of the problem

Density-functional theory in its earliest formulation by Hohenberg, Kohn and Sham [5, 8] aims at a description of the description of ground state properties of many-electron systems in terms of the electron density. One may wonder why this is possible. Let us therefore investigate this point more closely. Consider a Hamiltonian of a stationary many-body system

$$\hat{H}_v = \hat{T} + \hat{V} + \hat{W} \quad (1)$$

where  $\hat{T}$  is the kinetic energy of the electrons,  $\hat{V}$  the external potential, and  $\hat{W}$  the two-particle interaction. We denote the Hamilton operator  $\hat{H}_v$  with a subindex  $v$  to indicate that we will consider the Hamiltonian as a functional of the external potential  $v$ . The constituent terms are explicitly

given as

$$\hat{T} = \sum_{i=1}^N -\frac{1}{2}\nabla_i^2 \quad (2)$$

$$\hat{V} = \sum_{i=1}^N v(\mathbf{r}_i) \quad (3)$$

$$\hat{W} = \sum_{i>j}^N w(|\mathbf{r}_i - \mathbf{r}_j|) \quad (4)$$

where  $w(|\mathbf{r}|) = 1/|\mathbf{r}|$  will in our discussion always be the Coulomb potential. We are interested in electronic systems, i.e. molecules and solids. For all these systems the kinetic energy operator  $\hat{T}$  and two-particle interaction  $\hat{W}$  are identical. They only differ in the form of the external potential  $v(\mathbf{r})$  and the number of electrons  $N$ . The properties of all these systems can therefore be regarded as a functional of the external potential  $v$ . This is in particular the case for the ground state wavefunction  $|\Psi[v]\rangle$  and the ground state energy  $E[v]$ , which are of course related by the Schrödinger equation

$$(\hat{T} + \hat{V} + \hat{W})|\Psi[v]\rangle = E[v]|\Psi[v]\rangle \quad (5)$$

At first sight we have not gained much by this viewpoint, the problem looks as difficult as before. However, the problem will have a different appearance once we eliminate the potential in favor of the electron density. One may wonder what is so particular about the relation between the density and the potential. Let us therefore look specifically at the term which describes the external potential. It can be written as

$$\hat{V} = \int d^3r v(\mathbf{r}) \hat{n}(\mathbf{r}) \quad (6)$$

where we defined the density operator by

$$\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (7)$$

The expectation value of  $\hat{V}$  is given by

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d^3r n(\mathbf{r}) v(\mathbf{r}) \quad (8)$$

where  $n(\mathbf{r})$  the electron density. The electron density is obtained from the many-body wavefunction, which in our case will usually be the ground

state wavefunction of Hamiltonian  $\hat{H}_v$ , by

$$n(\mathbf{r}_1) = \langle \Psi | \hat{n}(\mathbf{r}_1) | \Psi \rangle = N \sum_{\sigma_1 \dots \sigma_N} \int d^3r_2 \dots d^3r_N |\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N)|^2 \quad (9)$$

In this expression  $\sigma_i$  is the spin variable for electron  $i$ . The physical interpretation of the density is that  $n(\mathbf{r})\Delta V$  is proportional to the probability of finding an electron in an infinitesimal volume  $\Delta V$  around  $\mathbf{r}$ . Note that in the definition Eq.(9) we sum over the spin coordinate  $\sigma_1$  so we do not distinguish between the probabilities of finding up or down spin electrons at  $\mathbf{r}$ . We see from Eq.(8) that the external potential  $v(\mathbf{r})$  and the electron density  $n(\mathbf{r})$  are conjugate variables. With this we mean that they occur as a simple product in the contribution of the external potential to the energy. It is exactly this property that allows us to prove the Hohenberg-Kohn theorem which establishes a 1-1-correspondence between the density and the external potential. We can therefore go from a functional  $E[v]$  of the external potential to a functional  $E[n]$  of the density. We can ask ourselves whether there is any reason that  $E[n]$  would be easier to calculate than  $E[v]$ . A priori there is no reason to expect this. However, we will see that the determination of  $E[n]$  is equivalent to the solution of a set of one-particle equations, known as the Kohn-Sham equations, with a potential  $v_s[n]$  that is also a functional of the density. By now we know that we can find practical and useful approximations for this potential  $v_s[n]$  and that the Kohn-Sham equations have been successfully applied to the calculation of properties of many electronic systems. However, as in any physical theory, there are a number of assumptions made in the transformation to the Kohn-Sham one-particle equations. The aim of this paper is to discuss these assumptions and thereby the validity of the Kohn-Sham equations.

### 3. Conditions on the electron density and the external potentials

We begin by giving a discussion of the properties of the two key objects in density functional theory, the density  $n$  and the external potential  $v$ . The density has the obvious properties

$$n(\mathbf{r}) \geq 0 \quad , \quad \int d^3r n(\mathbf{r}) = N \quad (10)$$

These properties follow directly from the definition of the density and the usual normalization condition on the wavefunction. If we take into account that the density is obtained as the density of a bound eigenstate of Hamiltonian (1) we can derive further conditions. For this we put the physical

constraint on the many-body system that it has a finite expectation value of the kinetic energy, i.e.

$$T[\Psi] = \frac{1}{2} \sum_{i=1}^N \sum_{\sigma_1 \dots \sigma_N} \int d^3 r_1 \dots d^3 r_N |\nabla_i \Psi|^2 < \infty \quad (11)$$

At this point it is useful to introduce a new space of functions. We say that a function  $f$  is in  $H^1(\mathcal{R}^n)$  ( $\mathcal{R}$  denotes the real numbers) if

$$\|f\| = \left( \int d^n \mathbf{r} (|f(\mathbf{r})|^2 + |\nabla f(\mathbf{r})|^2) \right)^{1/2} < \infty \quad (12)$$

The space of functions  $H^1(\mathcal{R}^n)$  is called a Sobolev space. The supindex 1 refers to the fact that the definition of the norm contains only first order derivatives. We therefore see that finiteness of the kinetic energy implies that  $\Psi$  is an element of the function space  $H^1(\mathcal{R}^{3N})$ . Differentiation of Eq.(9) and use of the Cauchy-Schwarz inequality then leads to [1]

$$(\nabla_1 n(\mathbf{r}_1))^2 \leq 4Nn(\mathbf{r}_1) \sum_{\sigma_1 \dots \sigma_N} \int d^3 r_2 \dots d^3 r_N |\nabla_1 \Psi|^2 \quad (13)$$

and hence

$$\frac{1}{2} \int d^3 r (\nabla \sqrt{n(\mathbf{r})})^2 \leq T[\Psi] < \infty \quad (14)$$

We see that the finiteness of the kinetic energy puts a constraint on the density. From Eq.(12) we see that  $\sqrt{n}$  belongs to  $H^1(\mathcal{R}^3)$ . We also see that if we consider systems with a finite kinetic energy, then we only need to consider the following set of densities

$$\mathcal{S} = \{n \mid n(\mathbf{r}) \geq 0, \sqrt{n} \in H^1(\mathcal{R}^3), \int d^3 r n(\mathbf{r}) = N\} \quad (15)$$

This set of densities has a property which will be of importance later, namely  $\mathcal{S}$  is convex. With this we mean that if  $n_1$  and  $n_2$  are elements of  $\mathcal{S}$ , then also  $\lambda n_1 + (1 - \lambda)n_2$  is an element of  $\mathcal{S}$  where  $0 \leq \lambda \leq 1$ . This property is easily proven using the Cauchy-Schwarz inequality. Now we will derive constraints on the allowed set of external potentials. In order to do this we introduce some other function spaces. We say that a given function  $f$  belongs to the space  $L^p$  if

$$\|f\|_p = \left( \int d^3 r |f(\mathbf{r})|^p \right)^{1/p} < \infty \quad (16)$$

Note that here we only consider functions on the usual threedimensional coordinate space  $\mathcal{R}^3$ . The letter  $L$  refers to Lebesgue integration, a feature

that assures that the function spaces are complete (complete normed spaces are also called Banach spaces). We will, however, not go into the detailed mathematics and refer the interested reader to the literature [4]. We just note that for continuous functions the integral is equivalent to the usual (Riemann) integral. Equation (16) defines a norm on the space  $L^p$  and we see from Eq.(10) that the density belongs to  $L^1$ . From the condition of finite kinetic energy and the use of a Sobolev inequality one can show that [1]

$$\int d^3r n^3(\mathbf{r}) \leq C \int d^3r (\nabla \sqrt{n(\mathbf{r})})^2 < \infty \quad (17)$$

where  $C = 3(\pi/2)^{4/3}$ . In other words, the finiteness of the kinetic energy implies that the density is also in the space  $L^3$ . Since we already know that  $n \in L^1$  we find that the density is element of the intersection of both spaces, i.e.  $n \in L^1 \cap L^3$ . We also see from the inequality (17) that  $\mathcal{S}$  is a subset of  $L^1 \cap L^3$ . Let us now see what this implies for the allowed set of external potentials when we require the expectation value of the external potential to be finite, i.e. we require

$$\left| \int d^3r n(\mathbf{r}) v(\mathbf{r}) \right| \leq \|nv\|_1 < \infty \quad (18)$$

If the potential is bounded, i.e.  $|v(\mathbf{r})| < M$  for some finite number  $M$  then

$$\left| \int d^3r n(\mathbf{r}) v(\mathbf{r}) \right| \leq \sup |v(\mathbf{r})| N < \infty \quad (19)$$

The space of bounded functions is called  $L^\infty$  and has the norm

$$\|f\|_\infty = \sup |f(\mathbf{r})| \quad (20)$$

The supremum is defined to be the smallest number  $M$  such that  $|f(\mathbf{r})| \leq M$  almost everywhere. The term 'almost everywhere' has a precise mathematical meaning for which we refer to the literature [4]. We almost never use it in the remainder of this paper. We therefore conclude that if  $v \in L^\infty$  then the expectation value of the external potential is finite. To show this we used that  $n \in L^1$ . But we also know that  $n \in L^3$  and if we make use of the Hölder inequality

$$\|fg\|_1 \leq \|f\|_p \|g\|_q \quad (21)$$

with  $1/p + 1/q = 1$  we obtain

$$\|nv\|_1 \leq \|n\|_3 \|v\|_{\frac{3}{2}} \quad (22)$$

which is finite if  $v \in L^{\frac{3}{2}}$ . Therefore the most general set of potentials for which the expectation value  $\langle \Psi | \hat{V} | \Psi \rangle$  is finite, is the set

$$L^{\frac{3}{2}} + L^\infty = \{v | v = u + w, u \in L^{\frac{3}{2}}, w \in L^\infty\} \quad (23)$$

i.e. the set of potentials that can be written as a sum of a function from  $L^{\frac{3}{2}}$  and a function from  $L^\infty$ . This is also a normed function space with norm

$$\|v\| = \inf\{\|u\|_{\frac{3}{2}} + \|w\|_\infty | v = u + w\} \quad (24)$$

In the remainder of this paper we will always consider the densities to be in the space  $L^1 \cap L^3$  and the potentials in the space  $L^{\frac{3}{2}} + L^\infty$ . It is important to note that the Coulomb potential is in the latter set since we can write

$$\frac{1}{|\mathbf{r}|} = \frac{\theta(1 - |\mathbf{r}|)}{|\mathbf{r}|} + \frac{\theta(|\mathbf{r}| - 1)}{|\mathbf{r}|} \quad (25)$$

where  $\theta$  is the Heaviside function,  $\theta(x) = 0$  if  $x \leq 0$  and  $\theta(x) = 1$  if  $x > 0$ . One can readily check that the first and the second term on the right hand side are in  $L^{\frac{3}{2}}$  and  $L^\infty$  respectively. One can easily extend this result to a finite sum of Coulomb potentials and therefore every molecule can be described with the potentials in the space  $L^{\frac{3}{2}} + L^\infty$ . One may finally wonder what the condition of finite Coulombic electron-electron repulsion, i.e.  $\langle \Psi | \hat{W} | \Psi \rangle < \infty$ , would imply for the density. However, one can show that if the kinetic energy  $\langle \Psi | \hat{T} | \Psi \rangle$  is finite then also  $\langle \Psi | \hat{W} | \Psi \rangle$  is finite [1], so this does not yield any new constraints on the density.

## 4. The Hohenberg-Kohn theorem

The basis of density-functional theory is provided by the Hohenberg-Kohn theorem [5]. We will provide a proof of this theorem for nondegenerate ground states. The case of degenerate ground states will be discussed later. The Hohenberg-Kohn theorem states that the density  $n(\mathbf{r})$  of a nondegenerate ground state uniquely determines the external potential  $v(\mathbf{r})$  up to an arbitrary constant. This means that the external potential is a well-defined functional  $v[n](\mathbf{r})$  of the density.

In the proof essential use is made of the fact that the density and the potential are conjugate variables. For the same reason we can, for instance, prove that the 2-particle interaction is a unique functional of the diagonal 2-particle density matrix. The general mapping between  $N$ -particle density matrices and  $N$ -body potentials is discussed by De Dominicis and Martin [6].

Let us consider the subset  $\mathcal{V} \subset L^{\frac{3}{2}} + L^\infty$  of potentials that yield a normalizable nondegenerate ground state. The solution of the Schrödinger equation provides us with a mapping from the external potential to the ground state wavefunction,  $v(\mathbf{r}) \rightarrow |\Psi[v]\rangle$ . Since we assume that we are dealing with nondegenerate ground states  $|\Psi[v]\rangle$  is uniquely determined apart from a trivial phase factor. We have therefore established a map  $C : \mathcal{V} \rightarrow \Phi$ , where  $\Phi$  is the set of ground states.



We will first prove that the map  $C$  is invertible. Suppose that  $|\Psi_1\rangle$  and  $|\Psi_2\rangle \in H^1(\mathcal{R}^{3N})$  correspond to external potentials  $v_1$  and  $v_2 \in L^\infty + L^{\frac{3}{2}}$  where  $v_1 \neq v_2 + C$ . We have to show that  $|\Psi_1\rangle \neq |\Psi_2\rangle$ . If we assume that  $|\Psi_1\rangle = |\Psi_2\rangle = |\Psi\rangle$  then by subtraction of the Hamiltonian for  $|\Psi_1\rangle$  and  $|\Psi_2\rangle$  we find that

$$(\hat{V}_1 - \hat{V}_2)|\Psi\rangle = (E_1 - E_2)|\Psi\rangle \quad (26)$$

If  $v_1 - v_2$  is not constant in some region then  $\Psi$  must vanish in this region for the above equation to be true. However if  $v_1, v_2 \in L^\infty + L^{\frac{3}{2}}$  then  $|\Psi\rangle$  cannot vanish on an open set (a set with nonzero measure) by the unique continuation theorem [1]. So we obtain a contradiction and hence we must have made a wrong assumption. Therefore  $|\Psi_1\rangle \neq |\Psi_2\rangle$  and we obtain the result that different potentials (differing more than a constant) give different wavefunctions. Consequently we find that the map  $C$  is invertible.

We now define the set  $\mathcal{A}$  as the set of densities which come from a nondegenerate ground state, where we only consider ground state densities from potentials in the set  $L^\infty + L^{\frac{3}{2}}$ . The set  $\mathcal{A}$  is obviously a subset of the previously defined set  $\mathcal{S}$ . From a given wavefunction in the set of ground states  $\Phi$  we can calculate the density according to Eq.(9). This provides us with a second map  $D : \Phi \rightarrow \mathcal{A}$  from ground state wavefunctions to ground state densities. Also this map is invertible. To show this we calculate

$$\begin{aligned} E[v_1] &= \langle \Psi[v_1] | \hat{T} + \hat{V}_1 + \hat{W} | \Psi[v_1] \rangle < \langle \Psi[v_2] | \hat{T} + \hat{V}_1 + \hat{W} | \Psi[v_2] \rangle \\ &= \langle \Psi[v_2] | \hat{T} + \hat{V}_2 + \hat{W} | \Psi[v_2] \rangle + \int n_2(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r}))d\mathbf{r} \\ &= E[v_2] + \int n_2(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r}))d\mathbf{r} \end{aligned} \quad (27)$$

Likewise we find

$$E[v_2] < E[v_1] + \int n_1(\mathbf{r})(v_2(\mathbf{r}) - v_1(\mathbf{r}))d\mathbf{r} \quad (28)$$

Adding both inequalities then yields the new inequality

$$\int d^3r (n_2(\mathbf{r}) - n_1(\mathbf{r}))(v_2(\mathbf{r}) - v_1(\mathbf{r})) < 0 \quad (29)$$

If we assume that  $n_1 = n_2$  then we obtain the contradiction  $0 < 0$  and we conclude that different ground states must yield different densities. Therefore the map  $D$  is also invertible. Consequently the map  $DC : \mathcal{V} \rightarrow \mathcal{A}$  is also invertible and the density therefore uniquely determines the external potential. This proves the Hohenberg-Kohn theorem.

Let us now pick an arbitrary density out of the set  $\mathcal{A}$  of densities of nondegenerate ground states. The Hohenberg-Kohn theorem then tells us that

there is a unique external potential  $v$  (to within a constant) and a unique ground state wavefunction  $|\Psi[n]\rangle$  (to within a phase factor) corresponding to this density. This also means that the ground state expectation value of any observable, represented by an operator  $\hat{O}$ , can be regarded as a density functional

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle \quad (30)$$

In particular we can thus define the Hohenberg-Kohn functional  $F_{HK}$  on the set  $\mathcal{A}$  as

$$F_{HK}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle \quad (31)$$

With this functional we can define the energy functional  $E_v$  as

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{HK}[n] \quad (32)$$

If  $n_0$  is a ground state density corresponding to external potential  $v_0$  and  $n$  an arbitrary other ground state density then

$$\begin{aligned} E_{v_0}[n] &= \int n(\mathbf{r})v_0(\mathbf{r})d\mathbf{r} + F_{HK}[n] = \langle \Psi[n] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n] \rangle \\ &\geq \langle \Psi[n_0] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[n_0] \rangle = E_{v_0}[n_0] \end{aligned} \quad (33)$$

Therefore

$$E[v] = \inf_{n \in \mathcal{A}} \left\{ \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{HK}[n] \right\} \quad (34)$$

and we see that the ground state energy of a many-body system can be obtained by minimization of a density functional. For application of this formula we have to know  $F_{HK}$  on the set  $\mathcal{A}$ . In practice it is, of course, impossible to calculate  $F_{HK}$  exactly on this set of densities. Instead one would prefer to make an explicit approximation for  $F_{HK}$  as is usually done within the Kohn-Sham scheme. Before we go into that let us first discuss some properties of  $F_{HK}$ . The functional  $F_{HK}$  is a convex functional, i.e. if  $n_1, n_2 \in \mathcal{A}$  and if  $\lambda_1 n_1 + \lambda_2 n_2 \in \mathcal{A}$  with  $0 \leq \lambda_1, \lambda_2 \leq 1$  and  $\lambda_1 + \lambda_2 = 1$  then

$$F_{HK}[\lambda_1 n_1 + \lambda_2 n_2] \leq \lambda_1 F_{HK}[n_1] + \lambda_2 F_{HK}[n_2] \quad (35)$$

This is readily proven. Suppose that the ground state densities  $n_1, n_2, \lambda_1 n_1 + \lambda_2 n_2 \in \mathcal{A}$  correspond to the external potentials  $v_1, v_2$  and  $v$ . Then

$$\begin{aligned} F_{HK}[n] &= \langle \Psi[n] | \hat{T} + \hat{V} + \hat{W} | \Psi[n] \rangle - \int d^3r n(\mathbf{r})v(\mathbf{r}) \\ &= \lambda_1 \langle \Psi[n_1] | \hat{H} | \Psi[n_1] \rangle + \lambda_2 \langle \Psi[n_2] | \hat{H} | \Psi[n_2] \rangle - \int d^3r n(\mathbf{r})v(\mathbf{r}) \\ &\leq \lambda_1 \langle \Psi[n_1] | \hat{T} + \hat{W} | \Psi[n_1] \rangle + \lambda_2 \langle \Psi[n_2] | \hat{T} + \hat{W} | \Psi[n_2] \rangle \end{aligned}$$

$$\begin{aligned}
& + \int (\lambda_1 n_1(\mathbf{r}) + \lambda_2 n_2(\mathbf{r})) v(\mathbf{r}) d^3 r - \int d^3 r n(\mathbf{r}) v(\mathbf{r}) \\
& = \lambda_1 F_{HK}[n_1] + \lambda_2 F_{HK}[n_2]
\end{aligned} \tag{36}$$

and we obtain the convexity of  $F_{HK}$ . Note, however, that the domain  $\mathcal{A}$  of  $F_{HK}$  does not need to be convex, i.e. if  $n_1, n_2 \in \mathcal{A}$  then not necessarily  $\lambda_1 n_1 + \lambda_2 n_2 \in \mathcal{A}$  with  $0 \leq \lambda_1, \lambda_2 \leq 1$  and  $\lambda_1 + \lambda_2 = 1$ . We will come back to this point later when we consider the differentiability of  $F_{HK}$ . Let us first collect our results in the form a theorem

**Theorem 1 (Hohenberg-Kohn)** *The density  $n$  corresponding to a non-degenerate ground state specifies the external potential  $v$  up to a constant and the ground state wavefunction  $|\Psi[n]\rangle$  up to a phase factor. Moreover,*

1. *Any ground state expectation value corresponding to an observable  $\hat{O}$  is a functional of the density according to*

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle$$

2. *The ground state energy of a system with a nondegenerate ground state and an external potential  $v$  can be obtained from*

$$E[v] = \inf_{n \in \mathcal{A}} \left\{ \int n(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + F_{HK}[n] \right\}$$

$$\text{where } F_{HK}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle.$$

3.  *$F_{HK}$  is convex*

We finally discuss an interesting consequence of the Hohenberg-Kohn theorem. Suppose that in Eq.(29) we take  $v_2 = v_1 + \epsilon \delta v$  where  $\delta v$  is not a constant. We therefore obtain potential  $v_2$  by a small perturbation from potential  $v_1$ . By means of perturbation theory we can then calculate the change in the density which gives

$$n_2(\mathbf{r}) = n_1(\mathbf{r}) + \epsilon \delta n(\mathbf{r}) + O(\epsilon^2) \tag{37}$$

where  $\delta n$  can be calculated from the static density response function  $\chi$

$$\delta n(\mathbf{r}) = \int d^3 r' \chi(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') \tag{38}$$

The properties and explicit form of  $\chi$  are described in more detail in a later section. Therefore

$$(v_2(\mathbf{r}) - v_1(\mathbf{r}))(n_2(\mathbf{r}) - n_1(\mathbf{r})) = \epsilon^2 \delta v(\mathbf{r}) \delta n(\mathbf{r}) + O(\epsilon^3) \tag{39}$$

If we insert this expression in Eq.(29) and divide by  $\epsilon^2 > 0$  then we obtain:

$$\int d^3r \delta v(\mathbf{r}) \delta n(\mathbf{r}) + O(\epsilon) < 0 \quad (40)$$

Now taking the limit  $\epsilon \rightarrow 0$  and expressing  $\delta n$  in terms of the response function we obtain

$$\int d^3r d^3r' \delta v(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') < 0 \quad (41)$$

This is true for an arbitrary nonconstant potential variation. We therefore see that the eigenvalues of  $\chi$ , when we regard  $\chi$  as an integral operator, are negative. Moreover we see that the only potential variation that yields a zero density variation is given by  $\delta v = C$  where  $C$  is a constant. This implies that  $\chi$  is invertable. We will go more closely into this matter in a later section where we will prove the same using the explicit form of the density response function.

## 5. Kohn-Sham theory by Legendre transforms

The method described in this section goes back to the work of De Dominicis and Martin [6]. This work discusses the relations between  $N$ -body potentials and  $N$ -particle density matrices, of which the density-potential relation to be discussed here is a special case. The ground state energy  $E[v]$  and wave function  $|\Psi[v]\rangle$  are considered to be functionals of the external potential through solving the time-independent Schrödinger equation

$$(\hat{T} + \hat{V} + \hat{W})|\Psi[v]\rangle = E[v]|\Psi[v]\rangle \quad (42)$$

where the two-particle interaction  $\hat{W}$  is kept fixed. From this equation we see that the ground state energy as a functional of the external potential  $v$  can also be written as

$$E[v] = \langle \Psi[v] | \hat{H}_v | \Psi[v] \rangle \quad (43)$$

Our goal is now to go from the potential as our basic variable, to a new variable, which will be the electron density. The deeper reason that this is possible is that the density and the potential are conjugate variables. With this we mean that the contribution of the external potential to the total energy is simply an integral of the potential times the density. We make use of this relation if we take the functional derivative of the energy functional  $E[v]$  with respect to the potential  $v$ :

$$\frac{\delta E}{\delta v(\mathbf{r})} = \langle \frac{\delta \Psi}{\delta v(\mathbf{r})} | \hat{H}_v | \Psi \rangle + \langle \Psi | \hat{H}_v | \frac{\delta \Psi}{\delta v(\mathbf{r})} \rangle + \langle \Psi | \frac{\delta \hat{H}_v}{\delta v(\mathbf{r})} | \Psi \rangle$$

$$\begin{aligned}
&= E[v] \frac{\delta}{\delta v(\mathbf{r})} \langle \Psi | \Psi \rangle + \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \\
&= \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = n(\mathbf{r})
\end{aligned} \tag{44}$$

where we used the Schrödinger equation  $\hat{H}_v |\Psi\rangle = E[v] |\Psi\rangle$  and the normalization condition  $\langle \Psi | \Psi \rangle = 1$ . Note that the equation above is nothing but a functional generalization of the well-known Hellmann-Feynman theorem [7]. Now we can go to the density as our basic variable by defining a Legendre transform

$$F[n] = E[v] - \int d^3r n(\mathbf{r}) v(\mathbf{r}) = \langle \Psi[v] | \hat{T} + \hat{W} | \Psi[v] \rangle \tag{45}$$

where  $v$  must now be regarded as a functional of  $n$ . The uniqueness of such a mapping is guaranteed by the Hohenberg-Kohn theorem [5]. The set of densities for which the functional  $F[n]$  is defined is the set of so-called  $v$ -representable densities. These are ground state densities for a Hamiltonian with external potential  $v$ . The question which constraints one has to put on a density to make sure that it is  $v$ -representable is known as the  $v$ -representability problem. We postpone a discussion of these matters to later sections. From  $\delta E / \delta v = n$  it follows immediately that

$$\frac{\delta F}{\delta n(\mathbf{r})} = -v(\mathbf{r}) \tag{46}$$

This is our first basic relation. In order to derive the Kohn-Sham equations we define the following energy functional for a system of noninteracting particles with external potential  $v_s$  and with ground state wave function  $|\Phi[v_s]\rangle$ :

$$E_s[v_s] = \langle \Phi[v_s] | \hat{T} + \hat{V}_s | \Phi[v_s] \rangle \tag{47}$$

with Legendre transform

$$F_s[n] = E[v_s] - \int d^3r n(\mathbf{r}) v_s(\mathbf{r}) = \langle \Phi[v_s] | \hat{T} | \Phi[v_s] \rangle \tag{48}$$

and derivatives

$$\frac{\delta E_s}{\delta v_s(\mathbf{r})} = n(\mathbf{r}) \tag{49}$$

$$\frac{\delta F_s}{\delta n(\mathbf{r})} = -v_s(\mathbf{r}) \tag{50}$$

We see that  $F_s[n]$  in Eq.(48) is the kinetic energy of a noninteracting system with potential  $v_s$  and density  $n$ . For this reason the functional  $F_s$  is usually

denoted by  $T_s$ . In the following we will adopt this notation. Finally we define the exchange-correlation functional  $E_{xc}[n]$  by the equation

$$F[n] = T_s[n] + \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + E_{xc}[n] \quad (51)$$

This equation assumes that the functionals  $F[n]$  and  $T_s[n]$  are defined on the same domain of densities. We thus assume that for a given ground state density of an interacting system there is a noninteracting system with the same density. In other words, we assume that the interacting density is noninteracting- $v$ -representable. If we differentiate Eq. (51) with respect to the density  $n$  we obtain

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3r' n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + v_{xc}(\mathbf{r}) \quad (52)$$

where

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \quad (53)$$

defines the exchange-correlation potential. Now the state  $|\Phi[v_s]\rangle$  is a ground state for a system of noninteracting particles, and can therefore be written as an antisymmetrized product of single-particle orbitals  $\varphi_i(\mathbf{r})$ . If we now collect our results we see that we have converted the ground state problem into the following set of equations

$$\begin{aligned} E[v] &= \sum_{i=1}^N -\frac{1}{2} \int d^3r \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \\ &+ \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + E_{xc}[n] \end{aligned} \quad (54)$$

$$\left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int d^3r' n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) + v_{xc}(\mathbf{r})\right) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad (55)$$

$$n(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \quad (56)$$

The above equations constitute the ground state Kohn-Sham equations [8]. These equations turn out to be of great practical use. If we can find a good approximation for the exchange-correlation energy, we can calculate the exchange-correlation potential  $v_{xc}$  and solve the orbital equations self-consistently. The density we find in this way can then be used to calculate the ground state energy of the system.

The exchange-correlation functional is often split up into an exchange functional  $E_x$  and a correlation functional  $E_c$  as

$$E_{xc}[n] = E_x[n] + E_c[n] \quad (57)$$

in which the exchange and correlation functionals are defined by

$$E_x[n] = \langle \Phi_s[n] | \hat{W} | \Phi_s[n] \rangle - \frac{1}{2} \int d^3r d^3r' n(\mathbf{r}) n(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|) \quad (58)$$

$$E_c[n] = \langle \Psi[n] | \hat{H}_v | \Psi[n] \rangle - \langle \Phi_s[n] | \hat{H}_v | \Phi_s[n] \rangle \quad (59)$$

In this equation  $|\Phi_s[n]\rangle$  is the Kohn-Sham wavefunction and  $|\Psi[n]\rangle$  the true ground state wavefunction of the interacting system with density  $n$ . Since the Kohn-Sham wavefunction is not a ground state wavefunction of the true system we see immediately from the variational principle that  $E_c < 0$ . We see also that the form of the exchange functional in terms of the Kohn-Sham orbitals is identical to that of the exchange energy within the well-known Hartree-Fock approximation. However, since the Kohn-Sham and Hartree-Fock orbitals differ, the value of  $E_x[n]$  is not equal to the Hartree-Fock exchange. We finally remark that splitting up  $E_{xc}$  into an exchange and a correlation part has several disadvantages. First of all, this splitting has only meaning if the ground state of the true or Kohn-Sham system is non-degenerate. We will later see that  $E_{xc}[n]$  is a well-defined functional even for degenerate ground states, but that exchange and correlation separately are ill-defined in that case. Secondly, there are many cases, notably molecular dissociation cases, where the exchange-only theory is a bad starting point for the treatment of correlation effects and for which it is much easier to find good approximations for the combined exchange-correlation functional.

In this section we gave a derivation of the Kohn-Sham equations. However, in this derivation we made a number of assumptions. We assumed that for every ground state density of an interacting system there is a noninteracting system which has the same density in its ground state. Secondly, we assumed that the density functionals were differentiable. This assumes that the values of the functionals change smoothly with changes in the density. In the following sections we will investigate to which extent these assumptions are justified.

## 6. Definition of the functional derivative

Let us start by defining what we mean with a functional derivative. The derivative we will talk about is what in the mathematical literature [9, 10, 11, 12, 13, 14] is referred to as a Gâteaux derivative. Let  $G : B \rightarrow \mathcal{R}$  be a functional from a normed function space  $B$  to the real numbers  $\mathcal{R}$ . If for every  $h \in B$  there exist a continuous linear functional  $\delta G / \delta f : B \rightarrow \mathcal{R}$  defined by:

$$\frac{\delta G}{\delta f}[h] = \lim_{\epsilon \rightarrow 0} \frac{G[f + \epsilon h] - G[f]}{\epsilon} \quad (60)$$

then  $\delta G/\delta f$  is called the Gâteaux derivative in  $f \in B$ . If the limit exists but the resulting functional of  $h$  is not linear or continuous then this limit is called a Gâteaux variation. Note that the definition of the Gâteaux derivative is very similar to the definition of the directional derivative in vector calculus where the linear functional corresponds to the inner product of the gradient vector with the vector which specifies the direction of the differentiation. Often the linear functional  $\delta G/\delta f$  can be written in the form

$$\frac{\delta G}{\delta f}[h] = \int d^3r g(\mathbf{r})h(\mathbf{r}) \quad (61)$$

If this is the case we write

$$g(\mathbf{r}) = \frac{\delta G}{\delta f(\mathbf{r})} \quad (62)$$

which we will call the functional derivative of  $G$ . Note further that although  $\delta G/\delta f$  specifies a linear functional when acting on  $h$ , the function  $g(\mathbf{r})$  depends in general on  $f$  in a nonlinear way. We also see that the set of functional derivatives on a function space  $B$  is equal to the set of continuous linear functionals on that space. This set is called the dual space of  $B$  and denoted  $B^*$ . For instance, the dual space of  $B = L^1 \cap L^3$  is known to be the space  $B^* = L^{\frac{3}{2}} + L^\infty$ . From this we see that if the derivative of a density functional defined on the set of densities  $L^1 \cap L^3$  exists then its derivative is in the set  $L^{\frac{3}{2}} + L^\infty$ .

Let us now mention a straightforward consequence of the definition of the Gâteaux derivative. Suppose that the functional  $G$  which we assume to be Gâteaux differentiable, has a minimum at  $f_0$ , i.e.  $G[f] \geq G[f_0]$  for all  $f \in B$ . Then the function

$$g(\epsilon) = G[f_0 + \epsilon h] \geq G[f_0] \quad (63)$$

has a minimum in  $\epsilon = 0$  and therefore the derivative of  $g(\epsilon)$  in  $\epsilon = 0$  vanishes. Thus

$$0 = \frac{dg}{d\epsilon}(0) = \lim_{\epsilon \rightarrow 0} \frac{g(\epsilon) - g(0)}{\epsilon} = \frac{\delta G}{\delta f}(f_0)[h] \quad (64)$$

Therefore a necessary condition for a differentiable functional for having a minimum at  $f_0$  is that its Gâteaux derivative vanishes at  $f_0$ . We further prove one other fact that we will use later. If  $G$  is a convex functional, i.e.

$$G[\lambda f_0 + (1 - \lambda)f_1] \leq \lambda G[f_0] + (1 - \lambda)G[f_1] \quad (65)$$

for  $0 \leq \lambda \leq 1$  then the function

$$g(\lambda) = G[f_0 + \lambda(f_1 - f_0)] \quad (66)$$



is a continuous function on the interval  $[0, 1]$ . To show this we will show that  $g(\lambda)$  is convex. Take  $\lambda_1, \lambda_2$  and  $\epsilon$  from the interval  $[0, 1]$ . Then

$$\begin{aligned} g(\epsilon\lambda_1 + (1 - \epsilon)\lambda_2) &= G[\epsilon(f_0 + \lambda_1(f_1 - f_0)) + (1 - \epsilon)(f_0 + \lambda_2(f_1 - f_0))] \\ &\leq \epsilon g(\lambda_1) + (1 - \epsilon)g(\lambda_2) \end{aligned} \quad (67)$$

Therefore  $g(\lambda)$  is a convex real function on the interval  $[0, 1]$  and hence continuous. The fact that convexity implies continuity is true for functions on the real axis, but this does not extend to infinite-dimensional spaces.

Let us finally make some remarks on higher order derivatives. If  $g(\epsilon) = G[f_0 + \epsilon h]$  defines a  $n$ -fold differentiable function of  $\epsilon$  then we define the  $n$ -th Gâteaux variation of  $G$  as

$$\frac{\delta^n G}{\delta f^n}[h, \dots, h] = \frac{d^n g}{d\epsilon^n}(0) \quad (68)$$

where  $\delta^n G/\delta f^n$  has now  $n$  arguments  $h$ . If this expression defines a multilinear continuous functional then we call this the  $n$ th-order Gâteaux derivative of  $G$ . For more details on this point we refer to reference [9]. Again, if this expression can be written in the form

$$\frac{\delta^n G}{\delta f^n}[h, \dots, h] = \int d^3 r_1 \dots d^3 r_n g(\mathbf{r}_1 \dots \mathbf{r}_n) h(\mathbf{r}_1) \dots h(\mathbf{r}_n) \quad (69)$$

then we call

$$\frac{\delta^n G}{\delta f(\mathbf{r}_1) \dots \delta f(\mathbf{r}_n)} = g(\mathbf{r}_1 \dots \mathbf{r}_n) \quad (70)$$

the  $n$ th-order functional derivative of  $G$ . So far our discussion has been rather abstract. Let us therefore apply the definition and calculate some functional derivatives.

## 7. Static linear response of the Schrödinger equation

We now consider the effect of small changes in the external field on the expectation values of physical observables. This is exactly what is studied in most experimental situations where one switches on and off an external field and studies how the system reacts to this. We will here study a more specific case in which we look at static changes in the external potential and their accompanying changes in the ground state expectation values. By investigating this problem we will learn how to take functional derivatives and how the existence of these derivatives is related to the existence of the linear response function.

Suppose that we have solved the following ground state problem:

$$\hat{H}|\Psi_0\rangle = (\hat{T} + \hat{V} + \hat{W})|\Psi_0\rangle = E_0|\Psi_0\rangle \quad (71)$$

where  $|\Psi_0\rangle$  is a nondegenerate ground state  $|\Psi[v]\rangle$  of Hamiltonian  $\hat{H}$  with external potential  $\hat{V}$ . From the wavefunction we can then calculate the expectation value of any operator  $\hat{O}$  which is a well-defined functional of the external potential

$$O[v] = \langle \Psi[v] | \hat{O} | \Psi[v] \rangle \quad (72)$$

Let us now calculate the functional derivative  $\delta O / \delta v$  at a given potential  $v$ . According to our definition in the previous section we have to calculate the quantity

$$\frac{\delta O}{\delta v}[\delta v] = \lim_{\epsilon \rightarrow 0} \frac{O[v + \epsilon \delta v] - O[v]}{\epsilon} \quad (73)$$

To evaluate this limit we have to calculate  $O[v + \epsilon \delta v]$  which we will do using static perturbation theory. We therefore make a slight change

$$\epsilon \delta \hat{V} = \epsilon \int d^3 r \hat{n}(\mathbf{r}) \delta v(\mathbf{r}) \quad (74)$$

in the external potential of Hamiltonian  $\hat{H}$ , i.e. we change the potential to  $\hat{V} + \epsilon \delta \hat{V}$ . The new ground state wavefunction which we will denote by  $|\Psi(\epsilon)\rangle$  satisfies

$$(\hat{H} + \epsilon \delta \hat{V}) |\Psi(\epsilon)\rangle = E(\epsilon) |\Psi(\epsilon)\rangle \quad (75)$$

We will solve this equation to first order in  $\epsilon$  with the condition  $|\Psi(0)\rangle = |\Psi_0\rangle$ . We note that the solution of Eq.(75) is not unique, because if  $|\Psi(\epsilon)\rangle$  is a solution then also  $|\Phi(\epsilon)\rangle = e^{i\theta(\epsilon)} |\Psi(\epsilon)\rangle$  is a solution, where  $\theta(\epsilon)$  is an arbitrary function of  $\epsilon$ . If we choose  $\theta(0) = 0$  then  $|\Phi(\epsilon)\rangle$  also satisfies the condition  $|\Phi(0)\rangle = |\Psi_0\rangle$ . The arbitrariness of the phase factor obviously does not affect the value of any expectation value, i.e.

$$O(\epsilon) = \langle \Psi(\epsilon) | \hat{O} | \Psi(\epsilon) \rangle = \langle \Phi(\epsilon) | \hat{O} | \Phi(\epsilon) \rangle \quad (76)$$

which is a unique function of  $\epsilon$ . However, it affects the appearance of our first order expansion, which for both functions looks like

$$|\Psi(\epsilon)\rangle = |\Psi_0\rangle + \epsilon |\Psi'(0)\rangle + O(\epsilon^2) \quad (77)$$

$$|\Phi(\epsilon)\rangle = |\Psi_0\rangle + \epsilon (|\Psi'(0)\rangle + i\theta'(0) |\Psi_0\rangle) + O(\epsilon^2) \quad (78)$$

where  $|\Psi'(0)\rangle$  and  $\theta'(0)$  are the first order derivatives of  $|\Psi(\epsilon)\rangle$  and  $\theta(\epsilon)$  in  $\epsilon = 0$ . We see that  $|\Psi(\epsilon)\rangle$  and  $|\Phi(\epsilon)\rangle$  differ in first order by the amount  $i\epsilon\theta'(0) |\Psi_0\rangle$ , i.e. by an imaginary number times the unperturbed ground state. This is exactly the freedom we will find in our expansion when we try to obtain the first order change in the wavefunction.

Let us expand the wavefunction and energy in Eq.(75) to first order in  $\epsilon$ . We then obtain

$$(\hat{H} - E_0) |\Psi'(0)\rangle = (E'(0) - \delta \hat{V}) |\Psi_0\rangle \quad (79)$$

where  $E'(0)$  is the first order derivative of  $E(\epsilon)$  in  $\epsilon = 0$ . To solve this equation we expand  $|\Psi'(0)\rangle$  in an orthonormal set of eigenstates of the unperturbed Hamiltonian  $\hat{H}$  as

$$|\Psi'(0)\rangle = \sum_{i=0}^{\infty} c_i |\Psi_i\rangle \quad (80)$$

If the unperturbed Hamiltonian has a continuous spectrum then for the corresponding energy eigenstates the summation in this equation has to be replaced by an integration. If we insert the expansion (80) into Eq.(79) for  $|\Psi'(0)\rangle$  we find the equation

$$\sum_{i=0}^{\infty} c_i (E_i - E_0) |\Psi_i\rangle = (E'(0) - \delta\hat{V}) |\Psi_0\rangle \quad (81)$$

where the energies  $E_i$  for  $i > 0$  are the eigenenergies of the excited states of the unperturbed Hamiltonian. If we multiply this equation from the left with  $\langle\Psi_0|$  we obtain for the change in energy

$$E'(0) = \langle\Psi_0|\delta\hat{V}|\Psi_0\rangle = \int d^3r n_0(\mathbf{r}) \delta v(\mathbf{r}) \quad (82)$$

where  $n_0$  is the density of the unperturbed system. We have therefore shown that

$$E'(0) = \lim_{\epsilon \rightarrow 0} \frac{E[v + \epsilon \delta v] - E[v]}{\epsilon} = \int d^3r n_0(\mathbf{r}) \delta v(\mathbf{r}) \quad (83)$$

As has been derived before we find  $\delta E / \delta v(\mathbf{r}) = n_0(\mathbf{r})$ . If we now multiply Eq.(81) from the left with  $\langle\Psi_k|$  for  $k > 0$  we find

$$c_k = - \frac{\langle\Psi_k|\delta\hat{V}|\Psi_0\rangle}{E_k - E_0} \quad (\text{for } k > 0) \quad (84)$$

Note that these coefficients are well-defined because  $E_k > E_0$ , since we are dealing with an isolated nondegenerate ground state. We therefore find for the first order change in the wavefunction

$$|\Psi'(0)\rangle = c_0 |\Psi_0\rangle - \sum_{k=1}^{\infty} \frac{|\Psi_k\rangle \langle\Psi_k|\delta\hat{V}|\Psi_0\rangle}{E_k - E_0} \quad (85)$$

The coefficient  $c_0$  remains undetermined by these equations. However, from the requirement that the perturbed system remains normalized we find

$$0 = \frac{d\langle\Psi|\Psi\rangle}{d\epsilon}(0) = \langle\Psi'(0)|\Psi_0\rangle + \langle\Psi_0|\Psi'(0)\rangle = c_0^* + c_0 \quad (86)$$

and hence  $c_0$  must be purely imaginary. This is exactly the kind of freedom in the first order wavefunction that we noted before. However, as we have seen this is related to choice of phase and does not affect the expectation values. We now want to calculate the first order change in an arbitrary expectation value due to a change  $\epsilon\delta v$  of the external potential. This change is given by

$$O'(0) = \lim_{\epsilon \rightarrow 0} \frac{O[v + \epsilon\delta v] - O[v]}{\epsilon} = \langle \Psi'(0) | \hat{O} | \Psi_0 \rangle + \langle \Psi_0 | \hat{O} | \Psi'(0) \rangle \quad (87)$$

where  $O'(0)$  is the derivative of  $O(\epsilon)$  in  $\epsilon = 0$  and where we assumed that the operator  $\hat{O}$  does not depend on  $\hat{V}$  (as for instance the Hamiltonian does). From Eq.(85) we obtain

$$\begin{aligned} O'(0) &= (c_0^* + c_0) \langle \Psi_0 | \hat{O} | \Psi_0 \rangle \\ &- \sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \delta \hat{V} | \Psi_k \rangle \langle \Psi_k | \hat{O} | \Psi_0 \rangle + \langle \Psi_0 | \hat{O} | \Psi_k \rangle \langle \Psi_k | \delta \hat{V} | \Psi_0 \rangle}{E_k - E_0} \end{aligned} \quad (88)$$

From the normalization condition Eq.(86) we see that the first term on the right hand side vanishes and we can rewrite the equation as

$$O'(0) = \frac{\delta O}{\delta v}[\delta v] = \int d^3r \frac{\delta O}{\delta v(\mathbf{r})} \delta v(\mathbf{r}) \quad (89)$$

where

$$\frac{\delta O}{\delta v(\mathbf{r})} = - \sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \hat{O} | \Psi_k \rangle \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{E_k - E_0} + c.c. \quad (90)$$

For a system with a nondegenerate ground state we therefore have obtained an explicit expression for the functional derivative  $\delta O/\delta v$  of the expectation value  $O[v]$ , evaluated at potential  $v(\mathbf{r})$ . We will use this formula later when we are studying functional derivatives with respect to the density.

## 8. Invertability of the density response function

In the previous section we obtained an expression for the functional derivative of an arbitrary expectation value. We now make a special choice for the operator  $\hat{O}$  and we choose  $\hat{O} = \hat{n}(\mathbf{r}')$ . In that case we obtain from Eq.(90):

$$\chi(\mathbf{r}', \mathbf{r}) = \frac{\delta n(\mathbf{r}')}{\delta v(\mathbf{r})} = - \sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}') | \Psi_k \rangle \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{E_k - E_0} + c.c. \quad (91)$$

where  $\chi(\mathbf{r}', \mathbf{r})$  is the static density response function. From this expression we see immediately that  $\chi$  is real and symmetric, i.e.  $\chi(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}', \mathbf{r})$ .

The density response function relates first order changes in the potential to first order changes in the density according to

$$\delta n(\mathbf{r}) = \int d^3 r' \chi(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') \quad (92)$$

If we change the potential by a constant then the density does not change. We therefore must have

$$\int d^3 r' \chi(\mathbf{r}, \mathbf{r}') = 0 \quad (93)$$

which can also be checked immediately from Eq.(91). Because of this property we also see that the induced density  $\delta n(\mathbf{r})$  automatically integrates to zero. The density response function has therefore indeed the physical properties that we expect. On the basis of the Hohenberg-Kohn theorem we may further expect that the only potential variation that yields a zero density variation is the constant potential, i.e. if

$$0 = \int d^3 r' \chi(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') \quad (94)$$

then  $\delta v(\mathbf{r}) = C$ . This readily proven from the properties of the response function. Suppose Eq.(94) is true for some  $\delta v(\mathbf{r}')$ . Then we obtain by integration with  $\delta v(\mathbf{r})$ :

$$0 = \int d^3 r d^3 r' \delta v(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') = -2 \sum_{k=1}^{\infty} \frac{|a_k|^2}{E_k - E_0} \quad (95)$$

where we defined  $a_k$  by

$$a_k = \int d^3 r \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle \delta v(\mathbf{r}) \quad (96)$$

Since  $E_k - E_0 > 0$  equation (95) can only be true if  $a_k = 0$  for all  $k \geq 1$ . But this implies that

$$\begin{aligned} 0 &= \sum_{k=1}^{\infty} a_k |\Psi_k\rangle = \sum_{k=1}^{\infty} \int d^3 r |\Psi_k\rangle \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle \delta v(\mathbf{r}) \\ &= \int d^3 r \delta v(\mathbf{r}) (1 - |\Psi_0\rangle \langle \Psi_0|) \hat{n}(\mathbf{r}) |\Psi_0\rangle \\ &= \int d^3 r \delta v(\mathbf{r}) (\hat{n}(\mathbf{r}) - n_0(\mathbf{r})) |\Psi_0\rangle \end{aligned} \quad (97)$$

where  $n_0(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle$  is the ground state density. Written in first quantization this implies that

$$\sum_{i=1}^N \Delta v(\mathbf{r}_i) |\Psi_0\rangle = 0 \quad (98)$$

where  $N$  is the number of electrons and  $\Delta v$  the potential

$$\Delta v(\mathbf{r}) = \delta v(\mathbf{r}) - \frac{1}{N} \int d^3r n_0(\mathbf{r}) \delta v(\mathbf{r}) \quad (99)$$

Now Eq.(98) implies that  $\Delta v(\mathbf{r}) = 0$  which together with Eq.(99) implies that  $\delta v(\mathbf{r}) = C$ . We have therefore shown that only constant potentials yield a zero-density variation, and therefore the density response function is invertible up to a constant. One should, however, be careful with what one means with the inverse response function. The response function defines a mapping  $\chi : \delta\mathcal{V} \rightarrow \delta\mathcal{A}$  from the set of potential variations from a nondegenerate ground state, which we call  $\delta\mathcal{V}$  and is a subset of  $L^{\frac{3}{2}} + L^\infty$ , to the set of first order densities variations, which we call  $\delta\mathcal{A}$ , that are produced by it. We have just shown that the inverse  $\chi^{-1} : \delta\mathcal{A} \rightarrow \delta\mathcal{V}$  is well-defined modulo a constant function. However, there are density variations that can never be produced by a potential variation and which are therefore not in the set  $\delta\mathcal{A}$ . An example of such a density variation is one which is identically zero on some finite volume.

From our analysis we can further derive another property of the static response function. Since  $\chi(\mathbf{r}, \mathbf{r}')$  is a real Hermitian integral kernel it has an orthonormal set of eigenfunctions which can be chosen to be real. Let  $f(\mathbf{r})$  be such an eigenfunction, i.e.

$$\int d^3r' \chi(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') = \lambda f(\mathbf{r}) \quad (100)$$

Multiplication from the right with  $f(\mathbf{r})$  and subsequent integration yields

$$\lambda \int d^3r f^2(\mathbf{r}) = \int d^3r d^3r' f(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') = -2 \sum_{k=1}^{\infty} \frac{|b_k|^2}{E_k - E_0} \leq 0 \quad (101)$$

where

$$b_k = \int d^3r \langle \Psi_k | \hat{n}(\mathbf{r}) | \Psi_0 \rangle f(\mathbf{r}) \quad (102)$$

We therefore find that  $\lambda \leq 0$ . However, we already know that  $\lambda = 0$  is only possible if  $f(\mathbf{r})$  is constant. We have therefore obtained the result that if a non-zero density variation is proportional to the potential that generates it, i.e.  $\delta n = \lambda \delta v$ , then the constant of proportionality  $\lambda$  is negative. This is exactly what one would expect on the basis of physical considerations. In actual calculations one indeed finds that the eigenvalues of  $\chi$  are negative. Moreover it is found that there is a infinite number of negative eigenvalues arbitrarily close to zero, which causes considerable numerical difficulties when one tries to obtain the potential variation that is responsible for a given density variation. We finally note the invertability proof for the static response function can be extended to the time-dependent case. For a recent review we refer to [15].

## 9. Functional derivatives and $v$ -representability

We are now ready to tackle the question how to calculate functional derivatives with respect to the density. By the Hohenberg-Kohn theorem every density associated with a nondegenerate ground state uniquely determines that ground state and the external potential that produced it. Because the density  $n$  determines the external potential  $v$  and vice versa we can parametrize the ground state either by the density or the external potential. The same is, of course, true for the expectation value of any operator  $\hat{O}$  that we calculate from the ground state. We will therefore write

$$O[n] = \langle \Psi[n] | \hat{O} | \Psi[n] \rangle = \langle \Psi[v] | \hat{O} | \Psi[v] \rangle = O[v] \quad (103)$$

Since we know how to calculate the functional derivative with respect to  $v$  the functional derivative with respect to  $n$  seems rather straightforward. By the chain rule for differentiation we obtain

$$\frac{\delta O}{\delta n(\mathbf{r})} = \int d^3 r' \frac{\delta O}{\delta v(\mathbf{r}')} \frac{\delta v(\mathbf{r}')}{\delta n(\mathbf{r})} = \int d^3 r' \frac{\delta O}{\delta v(\mathbf{r}')} \chi^{-1}(\mathbf{r}', \mathbf{r}) \quad (104)$$

where we used that the density response function has an inverse (modulo a constant). However, great care must be taken when deriving this equation. One needs to consider under which conditions the use of this chain rule is applicable. Let us therefore start with the definition of the functional derivative and try to calculate

$$\frac{\delta O}{\delta n}[\delta n] = \lim_{\epsilon \rightarrow 0} \frac{O[n_0 + \epsilon \delta n] - O[n_0]}{\epsilon} \quad (105)$$

where  $n_0$  is the density of a given nondegenerate ground state with external potential  $v_0$ . Now we run into the following problem. In order to make the value of  $O[n_0 + \epsilon \delta n]$  well-defined we have to make sure that  $n_0 + \epsilon \delta n \in \mathcal{A}$ , i.e. we have to make sure that this perturbed density belongs to a nondegenerate ground state. Whether or not this is true obviously depends on the choice we make for  $\delta n$ . A natural choice would be to take  $\delta n \in \delta \mathcal{A}$ , i.e. we take a  $\delta n$  from the set of first order density variations produced by some potential variations  $\delta v \in \delta \mathcal{V}$ . In this way we know that for every such  $\delta n$  there is a potential  $v_0 + \epsilon \delta v$  that generates, to first order in  $\epsilon$ , the required density. However, this still does not imply that  $n_0 + \epsilon \delta n \in \mathcal{A}$ . This will only be so if we can find an additional potential that would make the higher order terms in  $\epsilon$  disappear and it is not clear how to prove the existence of such a potential.

Nevertheless, this idea is sufficient to make a useful statement about the functional derivative. Let us therefore take some  $\delta n \in \delta \mathcal{A}$ . Then, by the

invertability of the density response function, there is a unique  $\delta v$  modulo a constant, such that

$$\delta n(\mathbf{r}) = \int d^3 r' \chi_0(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') \quad (106)$$

where  $\chi_0$  is the static density response function belonging to the nondegenerate ground state  $|\Psi_0\rangle$  with density  $n_0$ . Consider now the set of external potentials  $v_0 + \epsilon \delta v$ . For each  $\epsilon$  we can solve the Schrödinger equation and obtain a ground state density  $n_\epsilon(\mathbf{r})$ , which for  $\epsilon$  small enough will correspond to a nondegenerate ground state, i.e.  $n_\epsilon(\mathbf{r}) \in \mathcal{A}$ . By construction  $n_\epsilon - n_0$  will, to first order in  $\epsilon$ , be equal to the chosen  $\delta n$  we started with, i.e.  $n_\epsilon$  can be written as

$$n_\epsilon(\mathbf{r}) = n_0(\mathbf{r}) + \epsilon \delta n(\mathbf{r}) + m_\epsilon(\mathbf{r}) \in \mathcal{A} \quad (107)$$

where the term  $m_\epsilon(\mathbf{r})$  satisfies

$$\lim_{\epsilon \rightarrow 0} \frac{m_\epsilon(\mathbf{r})}{\epsilon} = 0 \quad (108)$$

Since  $n_\epsilon$  is the density of a nondegenerate ground state the expectation value  $O[n_\epsilon]$  is now well-defined and we can calculate

$$\lim_{\epsilon \rightarrow 0} \frac{O[n_\epsilon] - O[n_0]}{\epsilon} = \lim_{\epsilon \rightarrow 0} \frac{O[v_0 + \epsilon \delta v] - O[v_0]}{\epsilon} = \int d^3 r \frac{\delta O}{\delta v(\mathbf{r})} \delta v(\mathbf{r}) \quad (109)$$

We have therefore found a parametrized set of densities  $n_\epsilon \in \mathcal{A}$  for which the limit above is well-defined. Moreover, in this equation  $\delta v$  is uniquely defined by the  $\delta n \in \delta \mathcal{A}$  we started with by  $\delta v = \chi_0^{-1} \delta n$ , so that we can write

$$\lim_{\epsilon \rightarrow 0} \frac{O[n_0 + \epsilon \delta n + m_\epsilon] - O[n_0]}{\epsilon} = \int d^3 r \frac{\delta O}{\delta n(\mathbf{r})} \delta n(\mathbf{r}) \quad (110)$$

where the functional derivative  $\delta O / \delta n(\mathbf{r})$  is given (modulo a constant) by

$$\frac{\delta O}{\delta n(\mathbf{r})} = - \int d^3 r' \left( \sum_{k=1}^{\infty} \frac{\langle \Psi_0 | \hat{O} | \Psi_k \rangle \langle \Psi_k | \hat{n}(\mathbf{r}') | \Psi_0 \rangle}{E_k - E_0} + c.c. \right) \chi_0^{-1}(\mathbf{r}', \mathbf{r}) \quad (111)$$

Note that this derivative is defined up to a constant, since  $\delta n(\mathbf{r})$  integrates to zero. The functional derivative  $\delta O / \delta n[\delta n]$  in Eq.(110), regarded as a linear functional acting on  $\delta n$ , is of course independent of this constant. We have therefore a result that is in accordance with our naive expectation of Eq.(104). The functional derivative in Eq.(111) is well-defined in terms of the properties of the unperturbed system and independent of the choice for  $\delta n$ , and therefore independent of the parametrized path  $n_\epsilon \in \mathcal{A}$  that



we used to approach  $n_0$ . Moreover,  $n_\epsilon$  approaches the straight path  $n_0 + \epsilon \delta n$  arbitrarily closely for  $\epsilon \rightarrow 0$  and this is exactly the limit that we are interested in. We will therefore call the  $\delta O / \delta n$  of Eq.(111) the functional derivative of  $O[n]$ . Let us check that Eq.(111) gives us back some known results. Let us take  $\hat{O} = \hat{T} + \hat{W}$  so that  $O[n] = F_{HK}[n]$ . If we insert this operator in Eq.(111) we see that we have to calculate

$$\begin{aligned} \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_k \rangle &= \langle \Psi_0 | \hat{H}_0 - \hat{V}_0 | \Psi_k \rangle \\ &= E_k \delta_{k0} - \int d^3 r v_0(\mathbf{r}) \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_k \rangle \end{aligned} \quad (112)$$

where  $\hat{H}_0 = \hat{T} + \hat{V}_0 + \hat{W}$ . If we insert this matrix element into Eq.(111) we obtain:

$$\frac{\delta F_{HK}[n]}{\delta n(\mathbf{r})} = - \int d^3 r' d^3 r'' v_0(\mathbf{r}'') \chi_0(\mathbf{r}'', \mathbf{r}') \chi_0^{-1}(\mathbf{r}', \mathbf{r}) = -v_0(\mathbf{r}) \quad (113)$$

This is exactly the result that we derived earlier using Legendre transforms. We can, of course, also do this derivation for a noninteracting system where  $\hat{W} = 0$  and therefore  $\hat{O} = \hat{T}$ , in which case we obtain

$$\frac{\delta T_s}{\delta n(\mathbf{r})} = -v_s[n_0](\mathbf{r}) \quad (114)$$

where  $v_s[n_0]$  is the potential that in a noninteracting system generates density  $n_0$ , i.e. the Kohn-Sham potential corresponding to density  $n_0$ .

## 10. The Hohenberg-Kohn theorem for degenerate ground states

Until now we considered only nondegenerate ground states. These ground states have the simplifying feature that they are determined uniquely (up to a phase factor) by the external potential and therefore any expectation value calculated from the ground state wavefunction is a well-defined functional of the external potential  $v$ . However, degenerate ground states do occur (for instance in open shell atoms) and in that case the external potential does not generate a unique ground state but a linearly independent set of  $q$  different ground states. The expectation value of any operator (except the total energy) will then depend on which ground state out of the ground state manifold we choose to compute the expectation value from. This is in particular true for the density operator, and therefore different ground states  $|\Psi_i\rangle$  out of the ground state multiplet will yield different densities  $n_i$ . If we want to consider degenerate ground states, then the density is no longer a unique functional of the external potential. However, we will

show that the inverse mapping  $n \rightarrow v$  is well-defined, i.e. every ground state density determines uniquely the external potential that generated it. We will first generalize this statement somewhat. Instead of pure-state densities, which come from an eigenstate of the Hamiltonian  $\hat{H}$ , we will consider ensemble densities. To define this concept we first introduce for a  $q$ -fold degenerate ground state  $\{|\Psi_i\rangle, i = 1 \dots q\}$  the density matrix

$$\hat{D} = \sum_{i=1}^q \lambda_i |\Psi_i\rangle \langle \Psi_i| \quad \sum_{i=1}^q \lambda_i = 1 \quad (0 \leq \lambda_i \leq 1) \quad (115)$$

where the ground state wavefunctions  $|\Psi_i\rangle$  are chosen to be orthonormal. We then define the ground state expectation value of operator  $\hat{O}$  as

$$\langle O \rangle = \text{Tr} \hat{D} \hat{O} \quad (116)$$

where the trace operation for an arbitrary operator is defined as

$$\text{Tr} \hat{A} = \sum_{i=1}^{\infty} \langle \Phi_i | \hat{A} | \Phi_i \rangle \quad (117)$$

where  $\{|\Phi_i\rangle\}$  is an arbitrary complete set of states. The trace is independent of the complete set that we choose, as follows simply by insertion of a different complete set  $\{|\Psi_i\rangle\}$

$$\begin{aligned} \text{Tr} \hat{A} &= \sum_{i=1}^{\infty} \langle \Phi_i | \hat{A} | \Phi_i \rangle = \sum_{i,j=1}^{\infty} \langle \Phi_i | \hat{A} | \Psi_j \rangle \langle \Psi_j | \Phi_i \rangle \\ &= \sum_{i,j=1}^{\infty} \langle \Psi_j | \Phi_i \rangle \langle \Phi_i | \hat{A} | \Psi_j \rangle = \sum_{j=1}^{\infty} \langle \Psi_j | \hat{A} | \Psi_j \rangle \end{aligned} \quad (118)$$

If we choose the complete set to be the set of eigenstates of Hamiltonian  $\hat{H}$  then we find

$$\text{Tr} \hat{D} \hat{O} = \sum_{i=1}^{\infty} \langle \Psi_i | \hat{D} \hat{O} | \Psi_i \rangle = \sum_{i=1}^q \lambda_i \langle \Psi_i | \hat{O} | \Psi_i \rangle \quad (119)$$

This defines the expectation value of an observable  $\hat{O}$  in an ensemble described by density matrix  $\hat{D}$ . For the particular case of the density operator we have

$$n(\mathbf{r}) = \text{Tr} \hat{D} \hat{n}(\mathbf{r}) = \sum_{i=1}^q \lambda_i \langle \Psi_i | \hat{n}(\mathbf{r}) | \Psi_i \rangle = \sum_{i=1}^q \lambda_i n_i(\mathbf{r}) \quad (120)$$

We will denote densities  $n(\mathbf{r})$  of this type, which are obtained from an orthonormal set of ground states  $\{|\Psi_i\rangle, i = 1 \dots q\}$  corresponding to a potential  $v$ , as ensemble  $v$ -representable densities, or for short E-V-densities. We further denote the set of all E-V-densities generated by potentials in  $L^{\frac{3}{2}} + L^\infty$  as  $\mathcal{B}$ . A density will be called a pure state  $v$ -representable density or for short PS-V-density if it can be written as  $n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$ , where  $|\Psi\rangle$  is a ground state. Obviously PS-V-densities are special cases of E-V-densities and the set of PS-V-densities is therefore a subset of the set of E-V-densities.

We are now ready to formulate the Hohenberg-Kohn theorem for degenerate ground states: Every E-V-density determines the external potential that generated it up to an arbitrary constant. Let us make this statement a bit more specific. Suppose that  $\hat{D}_1$  and  $\hat{D}_2$  are density matrices belonging to ground state ensembles for potentials  $v_1$  and  $v_2$  respectively, with corresponding ensemble densities  $n_1$  and  $n_2$ . If  $v_1 \neq v_2 + C$  with  $C$  a constant, then  $n_1 \neq n_2$ . The proof is analogous to the proof of the nondegenerate case.

Suppose  $v_1$  generates the ground state multiplet  $A_1 = \{|\Phi_i\rangle, i = 1 \dots q_1\}$  and  $v_2$  generates the ground state multiplet  $A_2 = \{|\Psi_i\rangle, i = 1 \dots q_2\}$ . All the wavefunctions within these multiplets may, without loss of generality, be chosen orthonormal. Then none of the wavefunctions in the sets  $A_1$  and  $A_2$  are equal. This follows from the same argument as used in the proof of the Hohenberg-Kohn theorem for the nondegenerate case. In particular, as the sets  $A_1$  and  $A_2$  are only defined to within a unitary transformation no  $|\Psi_i\rangle$  in  $A_2$  is a linear combination of the  $|\Phi_i\rangle$  in  $A_1$ . This then implies that two ground state ensemble density matrices constructed from the ground states in  $A_1$  and  $A_2$  are different

$$\hat{D}_1 = \sum_{i=1}^{q_1} \lambda_i |\Phi_i\rangle \langle \Phi_i| \neq \sum_{i=1}^{q_2} \mu_i |\Psi_i\rangle \langle \Psi_i| = \hat{D}_2 \quad (121)$$

where  $\sum \lambda_i = \sum \mu_i = 1$ . This follows, for instance, by taking the inner product on both sides with  $|\Psi_m\rangle$  as the  $|\Psi_i\rangle$  are not linear combinations of the  $|\Phi_i\rangle$ . We have thus established that the sets of ground state density matrices for the two different potentials  $v_1$  and  $v_2$  are disjoint. We now have to prove that the density matrices in these sets yield different densities.

If  $\hat{H}_1 = \hat{T} + \hat{V}_1 + \hat{W}$  and  $\hat{H}_2 = \hat{T} + \hat{V}_2 + \hat{W}$  then

$$\text{Tr} \hat{D}_1 \hat{H}_2 > \text{Tr} \hat{D}_2 \hat{H}_2 \quad (122)$$

This follows directly from

$$\text{Tr} \hat{D}_1 \hat{H}_2 = \sum_{i=1}^{q_1} \lambda_i \langle \Phi_i | \hat{H}_2 | \Phi_i \rangle > \sum_{i=1}^{q_1} \lambda_i \langle \Psi_i | \hat{H}_2 | \Psi_i \rangle =$$

$$= \sum_{i=1}^{q_1} \lambda_i E[v_2] = E[v_2] = \sum_{i=1}^{q_2} \mu_i \langle \Psi_i | \hat{H}_2 | \Psi_i \rangle = \text{Tr} \hat{D}_2 \hat{H}_2 \quad (123)$$

We can now show that  $\hat{D}_1$  and  $\hat{D}_2$  yield different densities. We proceed again by reductio ad absurdum. We have

$$\begin{aligned} E[v_1] &= \text{Tr} \hat{D}_1 \hat{H}_1 = \text{Tr} \hat{D}_1 (\hat{H}_2 + \hat{V}_1 - \hat{V}_2) \\ &= \text{Tr} \hat{D}_1 \hat{H}_2 + \int n_1(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r})) d\mathbf{r} \\ &> \text{Tr} \hat{D}_2 \hat{H}_2 + \int n_1(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r})) d\mathbf{r} \\ &= E[v_2] + \int n_1(\mathbf{r})(v_1(\mathbf{r}) - v_2(\mathbf{r})) d\mathbf{r} \end{aligned} \quad (124)$$

Likewise we have

$$E[v_2] > E[v_1] + \int n_2(\mathbf{r})(v_2(\mathbf{r}) - v_1(\mathbf{r})) d\mathbf{r} \quad (125)$$

which added to the last inequality leads to

$$\int d^3r (n_2(\mathbf{r}) - n_1(\mathbf{r}))(v_2(\mathbf{r}) - v_1(\mathbf{r})) < 0 \quad (126)$$

This leads again to the contradiction  $0 < 0$  if we assume that  $n_1 = n_2$ . Therefore  $\hat{D}_1$  and  $\hat{D}_2$  must give different densities, which proves the theorem.

Within the set of ensemble ground state density matrices corresponding to the *same* potential however, two different density matrices can yield the same density. The simplest example is the hydrogen atom with the degenerate ground state wavefunctions for an electron with spin up and spin down, i.e.  $\Psi_\uparrow = (1s)\alpha$  and  $\Psi_\downarrow = (1s)\beta$  where  $\alpha$  and  $\beta$  are the spin wavefunctions. Both wavefunctions obviously have the same total density. Another example is provided by the two degenerate ground state wavefunctions  $(1s)^2 2p^+$  and  $(1s)^2 2p^-$  of the noninteracting lithium atom, where  $2p^\pm$  are  $p$ -orbitals with angular momentum quantum numbers  $l = \pm 1$ . Both wavefunctions lead to the same density

$$n(\mathbf{r}) = 2|\varphi_{1s}(\mathbf{r})|^2 + |\varphi_{2p^+}(\mathbf{r})|^2 = 2|\varphi_{1s}(\mathbf{r})|^2 + |\varphi_{2p^-}(\mathbf{r})|^2 \quad (127)$$

We have therefore constructed two degenerate ground states with the same density. As a consequence the ground state expectation value of a given operator may no longer be considered as a functional of the density (take, for instance, the expectation values of the spin and angular momentum in our examples). However, if two different ground state density matrices have

the same density then also the energy  $\text{Tr} \hat{D} \hat{H}$  for those different density matrices is the same. For every E-V-density  $n$  we can therefore unambiguously define the ensemble version of the  $F_{HK}$  functional as [16]

$$F_{EHK}[n] = \text{Tr} \hat{D}[n](\hat{T} + \hat{W}) \quad (128)$$

where  $\hat{D}[n]$  is any of the ground state ensemble density matrices corresponding to  $n$ . We can now define an extension of the energy functional  $E_v$  to the set of E-V-densities

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{EHK}[n] = \text{Tr} \hat{D}[n]\hat{H} \quad (129)$$

Similarly as for  $F_{HK}$  we easily can prove

$$E[v] = \inf_{n \in \mathcal{B}} \left\{ \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{EHK}[n] \right\} \quad (130)$$

The functional  $F_{EHK}$  is an extension of  $F_{HK}$  since

$$F_{EHK}[n] = F_{HK}[n] \text{ if } n \in \mathcal{A} \quad (131)$$

This follows directly from the fact that for a non-degenerate ground state  $|\Psi[n]\rangle$  corresponding to  $n$  we have  $\hat{D}[n] = |\Psi[n]\rangle\langle\Psi[n]|$ , so

$$F_{EHK}[n] = \text{Tr} \hat{D}[n](\hat{T} + \hat{W}) = \langle\Psi[n]|\hat{T} + \hat{W}|\Psi[n]\rangle = F_{HK}[n] \quad (132)$$

We can furthermore prove that  $F_{EHK}$  is convex by the same proof as for  $F_{HK}$ . Nothing is however known about the convexity of the set of E-V-densities  $\mathcal{B}$  itself which constitute the domain of  $F_{EHK}$ . Let us collect our results in the form of a theorem

**Theorem 2 (Hohenberg-Kohn)** *The E-V-density  $n$  specifies the external potential up to a constant. Moreover,*

1. *The ground state energy of a system with external potential  $v$  can be obtained from*

$$E[v] = \inf_{n \in \mathcal{B}} \left\{ \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{EHK}[n] \right\}$$

*where  $F_{EHK}[n] = \text{Tr} \hat{D}[n](\hat{T} + \hat{W})$  and  $\hat{D}[n]$  is a ground state density matrix with  $\text{Tr} \hat{D}[n]\hat{n}(\mathbf{r}) = n(\mathbf{r})$ .*

2.  *$F_{EHK}$  is convex*

As we will now demonstrate the subset of PS-V-densities of  $\mathcal{B}$  is not convex. More precisely, we will now show that there are E-V-densities which are not PS-V-densities [1, 17]. As any E-V-density is a convex combination of PS-V densities this then demonstrates the non-convexity of the set of PS-V-densities.

Consider an atom with total angular momentum quantum number  $L > 0$  which has a  $2L + 1$ -degenerate ground state. The external potential  $v$  is the spherically symmetric Coulomb potential of the atomic nucleus and the degeneracy is a result of rotational invariance of the Hamiltonian of the system. The ground state wavefunctions then transform among one another according to a  $2L + 1$ -dimensional unitary representation of the rotation group. We assume that there is no accidental degeneracy. If we denote the ground state wave functions by  $\{|\Psi[n_i]\rangle = |\Psi_i\rangle, i = 1 \dots 2L + 1\}$  and the corresponding electron densities by  $n_i$  then the following convex combination

$$\bar{n} = \frac{1}{2L + 1} \sum_{i=1}^{2L+1} n_i \quad (133)$$

is invariant under all rotations and therefore spherically symmetric. However the  $n_i$  are not spherical. In fact, there is no linear combination of the ground states  $|\Psi_i\rangle$  that leads to a spherically symmetric density. As the  $n_j$  is obtained from  $|\Psi_j\rangle$ , which by a unitary transformation can be obtained from any other  $|\Psi_i\rangle$ , and the external potential is invariant under rotations we find that

$$\int n_i(\mathbf{r})v(\mathbf{r})d\mathbf{r} = \int n_j(\mathbf{r})v(\mathbf{r})d\mathbf{r} = \int \bar{n}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (134)$$

for all  $0 \leq i, j \leq 2L + 1$ . Let us now suppose that  $\bar{n}$  is a ground state density obtained from a pure state wavefunction  $|\Psi[\bar{n}]\rangle$ . This wavefunction is not a linear combination of the  $|\Psi_i\rangle$  otherwise  $\bar{n}$  would not be spherically symmetric. We then find

$$\begin{aligned} F_{EHK}[\bar{n}] &= \langle \Psi[\bar{n}] | \hat{H}_v | \Psi[\bar{n}] \rangle - \int \bar{n}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \\ &> \sum_{i=1}^{2L+1} \frac{1}{2L+1} \langle \Psi[n_i] | \hat{H} | \Psi[n_i] \rangle - \int \bar{n}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \\ &= \sum_{i=1}^{2L+1} \frac{1}{2L+1} F_{EHK}[n_i] \end{aligned} \quad (135)$$

This then gives

$$F_{EHK}[\bar{n}] > \sum_{i=1}^{2L+1} \frac{1}{2L+1} F_{EHK}[n_i] \quad (136)$$

But we also know that  $F_{EHK}$  is convex on the set of E-V-densities. This leads to a contradiction and hence we must conclude that  $\bar{n}$  can not be a pure state density of any potential. The density  $\bar{n}$  is, however, a convex combination of ground state densities corresponding to the same external potential and therefore, by definition, an ensemble  $v$ -representable density. We therefore have constructed an E-V-density which is not a PS-V-density. For an explicit numerical example of such a density we refer to the work of Aryasetiawan and Stott [18].

## 11. Linear response for degenerate ground states and the differentiability of $F_{EHK}$

In the previous sections we learned to take functional derivatives on the basis of linear response theory. We concentrated on nondegenerate ground states for which the response functions are well-defined. We will now use response theory for degenerate ground states to study the differentiability of the functional  $F_{EHK}$ .

It is clear that in the case of degeneracy the expectation value of all observables, except the energy, depends on which particular ground state we choose to calculate the expectation value from. This poses a clear difficulty for the definition of general density functionals and their functional derivatives. One may, however, argue that if a potential  $v_0$  leads to a degenerate ground state then we can always find an arbitrarily small perturbation of the potential  $\epsilon\delta v$  that lifts the degeneracy and therefore the expectation value

$$O[v_0 + \epsilon\delta v] = \langle \Psi[v_0 + \epsilon\delta v] | \hat{O} | \Psi[v_0 + \epsilon\delta v] \rangle \quad (137)$$

of an observable described by an operator  $\hat{O}$  does exist for any  $\epsilon > 0$ , where  $|\Psi[v_0 + \epsilon\delta v]\rangle$  is the ground state wavefunction of the perturbed system. Therefore also the limit

$$\bar{O}[v_0, \delta v] = \lim_{\epsilon \rightarrow 0} O[v_0 + \epsilon\delta v] \quad (138)$$

is defined, although it will in general depend on the potential variation  $\delta v$ . One can therefore define the functional derivative as follows

$$O'[\delta v] = \lim_{\epsilon \rightarrow 0} \frac{O[v_0 + \epsilon\delta v] - \bar{O}[v_0, \delta v]}{\epsilon} \quad (139)$$

However, we will see that these derivatives depend in a nonlinear way on  $\delta v$  and are therefore only defined as Gâteaux variations rather than Gâteaux derivatives. We shall especially be interested in the case where  $\hat{O}$  is the density operator. For the energy the limit in Eq.(138) is independent of  $\delta v$  and we may wonder if a Gâteaux derivative still exists. Let us investigate

this in more detail. Suppose we have an Hamiltonian  $\hat{H}_0$  with external potential  $v_0$  which has a  $q$ -fold degenerate ground state. Let us now apply a perturbation  $\epsilon\delta v$  which lifts the degeneracy. Then there are  $q$  eigenstates  $\{|\Psi_k(\epsilon)\rangle, k = 1 \dots q\}$  with energies  $E_k(\epsilon)$  of the perturbed Hamiltonian that are continuously connected to degenerate ground states  $|\Psi_k(0)\rangle$  of the unperturbed Hamiltonian  $\hat{H}_0$ , i.e.

$$\lim_{\epsilon \rightarrow 0} |\Psi_k(\epsilon)\rangle = |\Psi_k(0)\rangle \quad (140)$$

with

$$E_k(0) = \langle \Psi_k(0) | \hat{H}_0 | \Psi_k(0) \rangle = E_0 \quad (141)$$

Note that since the states  $|\Psi_k(\epsilon)\rangle$  are orthonormal, also the limiting states  $|\Psi_k(0)\rangle$  in the degenerate ground state multiplet are orthonormal. Which particular ground states of the ground state manifold are reached by the  $\epsilon \rightarrow 0$  limit depends obviously on the form of the perturbation  $\delta v$ . In which way it depends on  $\delta v$  we will investigate now. The ground state wavefunctions  $|\Psi_k(\epsilon)\rangle$  satisfy the equation

$$(\hat{H}_0 + \epsilon\delta\hat{V} + \frac{\epsilon^2}{2}\delta\hat{U})|\Psi_k(\epsilon)\rangle = E_k(\epsilon)|\Psi_k(\epsilon)\rangle \quad (142)$$

where, for the later discussion, we also added a one-body potential  $\delta\hat{U}$  which is of second order in  $\epsilon$ . It turns out that this term influences the first order density response. We note, like in the nondegenerate case, that if  $|\Psi_k(\epsilon)\rangle$  is a solution to this equation then also  $|\Phi_k(\epsilon)\rangle = e^{i\theta_k(\epsilon)}|\Psi_k(\epsilon)\rangle$  is a solution, where  $\theta_k(\epsilon)$  is an arbitrary function of  $\epsilon$ . This freedom will, as in the nondegenerate case, not affect any of the expectation values. If we expand the Schrödinger equation (142) to first order in  $\epsilon$  we obtain

$$(\hat{H}_0 - E_0)|\Psi'_k(0)\rangle = (E'_k(0) - \delta\hat{V})|\Psi_k(0)\rangle \quad (143)$$

where  $E'_k(0)$  and  $|\Psi'_k(0)\rangle$  are the first order derivatives of  $E_k(\epsilon)$  and  $|\Psi_k(\epsilon)\rangle$  with respect to  $\epsilon$  in  $\epsilon = 0$ . In order to solve this equation for  $|\Psi'_k(0)\rangle$  we expand this quantity in the  $q$   $\epsilon$ -connected ground states and all the other eigenstates of  $\hat{H}_0$ , i.e.

$$|\Psi'_k(0)\rangle = \sum_{i=1}^{\infty} c_i^k |\Psi_i\rangle \quad (144)$$

where  $|\Psi_i\rangle = |\Psi_i(0)\rangle$  for  $i = 1 \dots q$  and the states  $\{|\Psi_i\rangle, i > q\}$  are eigenstates of  $\hat{H}_0$  with eigenenergies  $E_i > E_0$ . If we insert this expansion into the first order Schrödinger equation (143) we obtain the equation

$$\sum_{i=1}^{\infty} c_i^k (E_i - E_0) |\Psi_i\rangle = (E'_k(0) - \delta\hat{V}) |\Psi_k(0)\rangle \quad (145)$$



If we multiply this equation from the left with  $\langle \Psi_j |$  where  $1 \leq j \leq q$  we obtain

$$0 = E'_k(0)\delta_{jk} - \langle \Psi_j(0) | \delta \hat{V} | \Psi_k(0) \rangle \quad (146)$$

This is the equation tells us exactly how  $\delta v$  picks out the ground states in the degenerate multiplet. They are exactly the ones that diagonalize  $\delta \hat{V}$  within the  $q$ -dimensional space of degenerate ground state functions. This equation also tells us that

$$E'_k(0) = \langle \Psi_k(0) | \delta \hat{V} | \Psi_k(0) \rangle = \int d^3r n_k(\mathbf{r}) \delta v(\mathbf{r}) \quad (147)$$

If the state perturbed state with the lowest energy has label  $k = 1$  then we see that the functional derivative of the ground state energy is given as

$$\frac{\delta E}{\delta v(\mathbf{r})} = n_1(\mathbf{r}) \quad (148)$$

However, since  $n_1$  implicitly depends on the perturbation  $\delta v$  which picked out a particular ground state, this is not a proper Gâteaux derivative but only a Gâteaux variation. So even the energy functional has no functional derivative in the proper sense. Let us investigate the consequences for different expectation values. We therefore first have to determine the first order wavefunction. If we multiply Eq.(145) from the right with  $\langle \Psi_i |$  where  $i > q$  we obtain the coefficient  $c_i^k$  for  $i > q$  and the following expression for  $|\Psi'_k(0)\rangle$ :

$$|\Psi'_k(0)\rangle = \sum_{i=1}^q c_i^k |\Psi_i\rangle - \sum_{i=q+1}^{\infty} \frac{|\Psi_i\rangle \langle \Psi_i | \delta \hat{V} | \Psi_k(0) \rangle}{E_i - E_0} \quad (149)$$

However, the coefficients  $c_i^k$  for  $1 \leq i \leq q$  are not determined by Eq.(143). We know from the orthonormality of the states  $|\Psi_k(\epsilon)\rangle$  that

$$0 = \frac{d\langle \Psi_i | \Psi_k \rangle}{d\epsilon}(0) = \langle \Psi'_i(0) | \Psi_k(0) \rangle + \langle \Psi_i(0) | \Psi'_k(0) \rangle = c_k^{i*} + c_i^k \quad (150)$$

i.e. the coefficients  $c_i^k$  form an anti-Hermitian matrix. In particular we find that the coefficients  $c_k^k$  are purely imaginary. The value of these diagonal elements is undetermined by the Schrödinger equation as they are related to the arbitrary phase  $\theta_k(\epsilon)$  which we can choose for each  $|\Psi_k(\epsilon)\rangle$ . As in the nondegenerate case the value of any expectation value does not depend on the coefficients  $c_k^k$ . This leaves us with the determination of the off-diagonal terms  $c_i^k$  for  $i \neq k$ . These coefficients can be found by expanding Eq.(142) to second order in  $\epsilon^2$ . This yields

$$(\hat{H}_0 - E_0) |\Psi''_k(0)\rangle = 2(E'_k(0) - \delta \hat{V}) |\Psi'_k(0)\rangle + (E''_k(0) - \delta \hat{U}) |\Psi_k(0)\rangle \quad (151)$$

where  $|\Psi_k''(0)\rangle$  and  $E_k''(0)$  are the second order derivatives of  $|\Psi_k(\epsilon)\rangle$  and  $E_k(\epsilon)$  in  $\epsilon = 0$ . If we multiply this equation from the left with  $\langle\Psi_l(0)|$  where  $1 \leq l \leq q$  and use Eq.(146) and Eq.(149) then we obtain

$$\begin{aligned} 0 &= 2(E_k'(0) - E_l'(0))c_l^k + E_k''(0)\delta_{lk} - \langle\Psi_l(0)|\delta\hat{U}|\Psi_k(0)\rangle \\ &+ 2 \sum_{i=q+1}^{\infty} \frac{\langle\Psi_l(0)|\delta\hat{V}|\Psi_i\rangle\langle\Psi_i|\delta\hat{V}|\Psi_k(0)\rangle}{E_i - E_0} \end{aligned} \quad (152)$$

If we in this equation take  $k = l$  we obtain an expression for the energy to second order in  $\epsilon$ :

$$E_k''(0) = 2 \int d^3r d^3r' \delta v(\mathbf{r}) \chi_k(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') + \int d^3r n_k(\mathbf{r}) \delta u(\mathbf{r}) \quad (153)$$

where  $n_k$  is the density corresponding to  $|\Psi_k(0)\rangle$  and  $\chi_k$  the following function

$$\chi_k(\mathbf{r}, \mathbf{r}') = \sum_{i=q+1}^{\infty} \frac{\langle\Psi_k(0)|\hat{n}(\mathbf{r})|\Psi_i\rangle\langle\Psi_i|\hat{n}(\mathbf{r}')|\Psi_k(0)\rangle}{E_i - E_0} + c.c. \quad (154)$$

If, on the other hand, we take  $l \neq k$  we obtain our desired equation for the coefficients  $c_i^k$ :

$$\begin{aligned} c_l^k &= \frac{1}{2} \frac{\langle\Psi_l(0)|\delta\hat{U}|\Psi_k(0)\rangle}{E_k'(0) - E_l'(0)} \\ &+ \frac{1}{E_k'(0) - E_l'(0)} \sum_{i=q+1}^{\infty} \frac{\langle\Psi_l(0)|\delta\hat{V}|\Psi_i\rangle\langle\Psi_i|\delta\hat{V}|\Psi_k(0)\rangle}{E_i - E_0} \end{aligned} \quad (155)$$

We see that indeed  $c_l^{k*} = -c_k^l$  as expected. We have therefore completely determined the first order change in the wavefunction. Let us see what this implies for the observables. The first order change in the expectation value of an observable  $\hat{O}$  is given by

$$O'(0) = \langle\Psi_k(0)|\hat{O}|\Psi_k'(0)\rangle + c.c. \quad (156)$$

If we insert our expression for the first order change in the wavefunction we obtain

$$\begin{aligned} O'(0) &= \int d^3r \zeta_k(\mathbf{r}) \delta v(\mathbf{r}) + \frac{1}{2} \int d^3r \eta_k(\mathbf{r}) \delta u(\mathbf{r}) \\ &+ \int d^3r d^3r' \xi_k(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}) \delta v(\mathbf{r}') \end{aligned} \quad (157)$$

where we defined the following functions

$$\zeta_k(\mathbf{r}) = \sum_{i=q+1}^{\infty} \frac{\langle \Psi_k(0) | \hat{O} | \Psi_i \rangle \langle \Psi_i | \hat{n}(\mathbf{r}) | \Psi_k(0) \rangle}{E_i - E_0} + c.c. \quad (158)$$

$$\eta_k(\mathbf{r}) = \sum_{l=1(l \neq k)}^q \frac{\langle \Psi_k(0) | \hat{O} | \Psi_l \rangle \langle \Psi_l | \hat{n}(\mathbf{r}) | \Psi_k(0) \rangle}{E'_k(0) - E'_l(0)} + c.c. \quad (159)$$

$$\xi_k(\mathbf{r}, \mathbf{r}') = \sum_{l=1}^q \sum_{i=q+1}^{\infty} \frac{\langle \Psi_k(0) | \hat{O} | \Psi_l \rangle \langle \Psi_l | \hat{n}(\mathbf{r}) | \Psi_i \rangle \langle \Psi_i | \hat{n}(\mathbf{r}') | \Psi_k(0) \rangle}{(E'_k(0) - E'_l(0))(E_i - E_0)} \quad (160)$$

If we choose  $\hat{O} = \hat{n}(\mathbf{r}'')$  then we obtain an expression for the first order change in the density

$$\begin{aligned} \delta n_k(\mathbf{r}'') &= \int d^3r \chi_k(\mathbf{r}'', \mathbf{r}) \delta v(\mathbf{r}) + \frac{1}{2} \int d^3r \eta_k(\mathbf{r}'', \mathbf{r}) \delta u(\mathbf{r}) \\ &+ \int d^3r d^3r' \xi_k(\mathbf{r}'', \mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}) \delta v(\mathbf{r}') \end{aligned} \quad (161)$$

where the functions  $\chi_k$ ,  $\eta_k$  and  $\xi_k$  are obtained by inserting  $\hat{n}(\mathbf{r}'')$  for  $\hat{O}$  in Eqns.(158), (159) and (160). If we denote the perturbed state with label  $k = 1$  as the one with the lowest energy then  $\delta n_1$  represents the change in ground state density. We see that this density change does not depend linearly on the first order change  $\delta v$  in the potential and even the second order change  $\delta u$  of the potential contributes to its value. Let us now take  $\delta u = 0$  and write

$$\begin{aligned} \delta n_1(\mathbf{r}'') &= \int d^3r \chi_1(\mathbf{r}'', \mathbf{r}) \delta v(\mathbf{r}) \\ &+ \int d^3r d^3r' \xi_1(\mathbf{r}'', \mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}) \delta v(\mathbf{r}') \end{aligned} \quad (162)$$

We can ask ourselves the question whether a given first order variation  $\delta n_1$  uniquely determines the first order density change  $\delta v$ . One can show from the Hohenberg-Kohn theorem for degenerate states that this is indeed the case. If we in Eq.(126) take  $v_2 = v_1 + \epsilon \delta v(\mathbf{r})$  where  $\delta v$  is not a constant function we obtain

$$\epsilon^2 \int d^3r \delta n_1(\mathbf{r}) \delta v(\mathbf{r}) + O(\epsilon^3) < 0 \quad (163)$$

Dividing by  $\epsilon^2$  and taking the limit  $\epsilon \rightarrow 0$  then yields

$$\int d^3r \delta n_1(\mathbf{r}) \delta v(\mathbf{r}) < 0 \quad (164)$$

We see that the first order density change  $\delta n_1$  can not be zero if  $\delta v$  is not a constant. In contrast to the nondegenerate case Eq.(164) does not imply that the function  $\chi_1$  is invertable, only the relation in Eq.(162) is invertable where the inverse only exists on the set of  $v$ -representable density variations within the set  $\mathcal{B}$ .

Let us now see what the linear response theory can tell us about the differentiability of  $F_{EHK}$ . We consider again a system with a degenerate ground state and external potential  $v_0$ . Let us take out of the set of ground state ensemble densities for this system a particular density  $n_0$ . We may then wonder whether the following limit

$$\frac{\delta F_{EHK}}{\delta n}[\delta n] = \lim_{\epsilon \rightarrow 0} \frac{F_{EHK}[n_0 + \epsilon \delta n] - F_{EHK}[n_0]}{\epsilon} \quad (165)$$

exists. For this limit to be well-defined we have to make sure that  $n_0 + \epsilon \delta n \in \mathcal{B}$  and we run into the same problem as for the nondegenerate case. However, in the nondegenerate case we could solve this difficulty using response theory. We will do the same for the degenerate case, but we will see that some difficulties remain. Suppose we look at the perturbed system with potential  $v_0 + \epsilon \delta v$  in which the degeneracy is lifted. For this system there is a well-defined ground state density  $n_\epsilon = n[v_0 + \epsilon \delta v]$ . From response theory we know that we can write  $n_\epsilon$  as

$$n_\epsilon(\mathbf{r}) = n_1(\mathbf{r}) + \epsilon \delta n_1(\mathbf{r}) + m_\epsilon(\mathbf{r}) \quad (166)$$

where

$$n_1(\mathbf{r}) = \lim_{\epsilon \rightarrow 0} n[v_0 + \epsilon \delta v] \quad (167)$$

$$0 = \lim_{\epsilon \rightarrow 0} \frac{m_\epsilon(\mathbf{r})}{\epsilon} \quad (168)$$

and where  $\delta n_1$  is explicitly given in Eq.(162). Now by construction the density  $n_\epsilon$  is in  $\mathcal{B}$  for all values of  $\epsilon$ . We can now consider the limit

$$\begin{aligned} \frac{\delta F_{EHK}}{\delta n}[\delta n_1] &= \lim_{\epsilon \rightarrow 0} \frac{F_{EHK}[n_1 + \epsilon \delta n_1 + m_\epsilon] - F_{EHK}[n_1]}{\epsilon} \\ &= \lim_{\epsilon \rightarrow 0} \frac{F_{EHK}[v_0 + \epsilon \delta v] - \bar{F}_{EHK}[v_0, \delta v]}{\epsilon} \end{aligned} \quad (169)$$

where  $\bar{F}_{EHK}[v_0, \delta v]$  is defined as in Eq.(138). The latter limit is readily calculated by inserting  $\hat{T} + \hat{W} = \hat{H}_0 - \hat{V}_0$  for the operator  $\hat{O}$  in Eqns.(158) and (160). We obtain for the first order change of  $F_{EHK}$

$$\delta F_{EHK} = - \int d^3r d^3r'' v_0(\mathbf{r}'') \chi_1(\mathbf{r}'', \mathbf{r}) \delta v(\mathbf{r})$$

$$\begin{aligned}
& - \int d^3r d^3r' d^3r'' v_0(\mathbf{r}'') \xi_1(\mathbf{r}'', \mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}) \delta v(\mathbf{r}') \\
& = - \int d^3r v_0(\mathbf{r}) \delta n_1(\mathbf{r})
\end{aligned} \tag{170}$$

and we thus obtain

$$\lim_{\epsilon \rightarrow 0} \frac{F_{EHK}[n_1 + \epsilon \delta n_1 + m_\epsilon] - F_{EHK}[n_1]}{\epsilon} = - \int d^3r v_0(\mathbf{r}) \delta n_1(\mathbf{r}) \tag{171}$$

We see that this limit is linear in  $\delta n_1$  and that furthermore  $v_0$  is independent of  $\delta n_1$ . Therefore we can write for the functional derivative of  $F_{EHK}$  in  $n_1$ :

$$\frac{\delta F_{EHK}}{\delta n(\mathbf{r})}(n_1) = -v_0(\mathbf{r}) \tag{172}$$

up to an arbitrary constant. However, we see that this derivative only exists for some special set of ground state densities corresponding to potential  $v_0$ . The derivative exists for those ground state densities that correspond to pure states that can be obtained in the  $\epsilon \rightarrow 0$  limit for a perturbed system with potential  $v_0 + \epsilon \delta v$ . It is not clear how to take the functional derivative at an arbitrary ensemble density  $n_0$  for potential  $v_0$ . We saw that there exist E-V-densities that are not PS-V-densities. If we consider an ensemble corresponding to such a density and change the external potential to  $v_0 + \epsilon \delta v$  where  $\delta v$  lifts the degeneracy then for  $\epsilon > 0$  the ensemble will change into a pure state and the density will change abruptly. We must therefore conclude that for general E-V-densities the functional derivative of  $F_{EHK}$  does not exist. This poses not only a theoretical problem but also a practical one. As we will discuss later, it is known from numerical investigations that there are ground state densities of interacting systems that are not pure state densities for a noninteracting system and therefore there is a clear need for establishing a Kohn-Sham scheme for arbitrary E-V-densities. Fortunately it turns out that one can define an extension of the functional  $F_{EHK}$  to a larger domain of densities which can be shown to be differentiable at the set of all E-V-densities. This functional is the Lieb functional  $F_L$  and will be studied in the next section.

## 12. The Levy and Lieb functionals $F_{LL}[n]$ and $F_L[n]$

The functionals  $F_{HK}$  and  $F_{EHK}$  have the unfortunate mathematical difficulty that their domains of definition  $\mathcal{A}$  and  $\mathcal{B}$ , although they are well-defined, are difficult to characterize, i.e. it is difficult to know if a given density  $n$  belongs to  $\mathcal{A}$  or  $\mathcal{B}$ . It is therefore desirable to extend the domains of definition of  $F_{HK}$  and  $F_{EHK}$  to an easily characterizable (preferably

convex) set of densities. This can be achieved using the constrained search procedure introduced by Levy [19]. We define the Levy-Lieb functional  $F_{LL}$  as

$$F_{LL}[n] = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \quad (173)$$

where the infimum is searched over all normalized anti-symmetric  $N$ -particle wave functions in  $H^1(\mathcal{R}^{3N})$  yielding density  $n$ . As shown earlier such a density is always in the convex set  $\mathcal{S}$  which is again a subspace of  $L^1 \cap L^3$ . One can furthermore show, as has been done by Simon [1], that the infimum is always a minimum, i.e. there is always a minimizing wave function. As this is the first important result that we obtain for  $F_{LL}$  we put it in the form of a theorem

**Theorem 3** *For any  $n \in \mathcal{S}$  there is a  $|\Psi[n]\rangle \in H^1(\mathcal{R}^{3N})$  such that*

$$F_{LL}[n] = \langle \Psi[n] | \hat{T} + \hat{W} | \Psi[n] \rangle$$

Let us discuss some properties of  $F_{LL}$ . The functional  $F_{LL}$  is an extension of the Hohenberg-Kohn functional  $F_{HK}$ , which is defined on  $\mathcal{A}$ , to the larger set  $\mathcal{S}$ , i.e

$$F_{LL}[n] = F_{HK}[n] \quad \text{if } n \in \mathcal{A} \quad (174)$$

This is readily derived. Suppose  $n$  is some ground state density corresponding to some external potential  $v$  and ground state  $|\Psi[n]\rangle$  then

$$\begin{aligned} \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{HK}[n] &= \langle \Psi[n] | \hat{H} | \Psi[n] \rangle = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle = \\ \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \inf_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle &= \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{LL}[n] \end{aligned} \quad (175)$$

We define a corresponding energy functional

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{LL}[n] \quad (176)$$

If  $n_0$  is the ground state density for potential  $v$  with corresponding ground state wave function  $\Psi[n_0]$  then

$$E_v[n] = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle \geq \langle \Psi[n_0] | \hat{H} | \Psi[n_0] \rangle = E_v[n_0] \quad (177)$$

Minimizing  $E_v$  over the set  $\mathcal{S}$  therefore yields the ground state density  $n_0$  corresponding to external potential  $v$ . The functional  $F_{LL}$  has however the inconvenient property that it is not convex.

**Theorem 4** *The functional  $F_{LL}$  is not convex*

To show this we take the example of a previous section where we presented a density  $\bar{n}$  which did not correspond to a ground state wavefunction. It was a convex combination of  $2L + 1$  degenerate ground state densities  $n_i$  with corresponding ground states  $|\Psi[n_i]\rangle$  for an external potential  $v$ . Then we find

$$\begin{aligned} \int \bar{n}(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{LL}[\bar{n}] &= \inf_{\Psi \rightarrow \bar{n}} \langle \Psi | \hat{H} | \Psi \rangle \\ &> \frac{1}{2L+1} \sum_{i=1}^{2L+1} \langle \Psi[n_i] | \hat{H} | \Psi[n_i] \rangle = \frac{1}{2L+1} \sum_{i=1}^{2L+1} F_{LL}[n_i] + \int \bar{n}(\mathbf{r})v(\mathbf{r})d\mathbf{r} \end{aligned} \quad (178)$$

and we find

$$F_{LL}[\bar{n}] > \frac{1}{2L+1} \sum_{i=1}^N F_{LL}[n_i] \quad (179)$$

which proves the non-convexity of  $F_{LL}$ . This is somewhat unfortunate as convexity is an important property which can be used to derive differentiability of functionals. We will therefore now define a different but related convex functional with the same domain  $\mathcal{S}$ . This is the Lieb functional  $F_L$  defined as

$$F_L[n] = \inf_{\hat{D} \rightarrow n} \text{Tr} \hat{D}(\hat{T} + \hat{W}) \quad (180)$$

where the infimum is searched over all  $N$ -particle density matrices

$$\hat{D} = \sum_{i=1} \lambda_i |\Psi_i\rangle \langle \Psi_i| \quad \sum_{i=1} \lambda_i = 1 \quad |\Psi_i\rangle \in H^1(\mathcal{R}^{3N}) \quad (181)$$

which yield the given density  $n(\mathbf{r}) = \text{Tr} \hat{D} \hat{n}(\mathbf{r})$  where  $\{|\Psi_i\rangle\}$  is an orthonormal set. Also for this case one can prove the infimum to be a minimum, i.e. there is a minimizing density matrix. We put the result again in the form of a theorem

**Theorem 5** *For every  $n \in \mathcal{S}$  there is a density matrix  $\hat{D}[n]$  such that*

$$F_L[n] = \text{Tr} \hat{D}[n](\hat{T} + \hat{W})$$

For the proof of this theorem we again refer to Lieb [1]. The functional  $F_L$  is an extension of  $F_{EHK}$  to the larger set  $\mathcal{S}$ , that is

$$F_L[n] = F_{EHK}[n] \quad \text{if } n \in \mathcal{B} \quad (182)$$

This follows directly from the fact that if  $n \in \mathcal{B}$  then there is a potential  $v$  which generates a ground state ensemble density matrix  $\hat{D}[n]$  which yields

$n$ . So

$$\begin{aligned}
\int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{EHK}[n] &= \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \text{Tr}\hat{D}[n](\hat{T} + \hat{W}) \\
&= \text{Tr}\hat{D}[n]\hat{H} = \inf_{\hat{D} \rightarrow n} \text{Tr}\hat{D}\hat{H} \\
&= \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_L[n]
\end{aligned} \tag{183}$$

We can again define an energy functional

$$E_v[n] = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_L[n] \tag{184}$$

which by a similar proof as for  $F_{LL}$  assumes its minimum at the ground state density corresponding to potential  $v$ . We further have the following relations

$$F_L[n] = F_{LL}[n] \text{ if } n \in \mathcal{A} \tag{185}$$

and

$$F_L[n] < F_{LL}[n] \text{ if } n \in \mathcal{B} \text{ and } n \notin \mathcal{A} \tag{186}$$

The first relation follows from the fact that if the density  $n$  is a pure state  $v$ -representable density then the minimizing density matrix for  $F_L$  is a pure state density matrix. The second relation also easily follows. We take  $n$  to be an E-V-density which is not a PS-V density. There is a ground state ensemble density matrix  $\hat{D}[n]$  for which we have

$$\int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_L[n] = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \text{Tr}\hat{D}[n](\hat{T} + \hat{W}) = \langle \Psi_i | \hat{H} | \Psi_i \rangle \tag{187}$$

where  $|\Psi_i\rangle$  is any of the ground states in the degenerate ground state multiplet. Any wave function yielding density  $n$  can not be a linear combination of these ground state wave-functions otherwise  $n$  would be pure state  $v$ -representable. Therefore its expectation value with the Hamiltonian must be larger, i.e

$$\langle \Psi_i | \hat{H} | \Psi_i \rangle < \inf_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle = \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} + F_{LL}[n] \tag{188}$$

which proves our statement.

We will now demonstrate another important property of  $F_L$ , which is its convexity.

**Theorem 6** *The functional  $F_L$  is convex*



This is easily shown. If  $n = \lambda_1 n_1 + \lambda_2 n_2$  with  $\lambda_1 + \lambda_2 = 1$  and  $0 \leq \lambda_1, \lambda_2 \leq 1$  then we have

$$\begin{aligned}
\lambda_1 F_L[n_1] + \lambda_2 F_L[n_2] &= \lambda_1 \inf_{\hat{D}_1 \rightarrow n_1} \text{Tr} \hat{D}_1 (\hat{T} + \hat{W}) \\
&+ \lambda_2 \inf_{\hat{D}_2 \rightarrow n_2} \text{Tr} \hat{D}_2 (\hat{T} + \hat{W}) \\
&= \inf_{\hat{D}_1, \hat{D}_2 \rightarrow n_1, n_2} \text{Tr} (\lambda_1 \hat{D}_1 + \lambda_2 \hat{D}_2) (\hat{T} + \hat{W}) \\
&\geq \inf_{\hat{D} \rightarrow n} \text{Tr} \hat{D} (\hat{T} + \hat{W}) = F_L[n] \quad (189)
\end{aligned}$$

We therefore now have established that  $F_L$  is a convex functional on a convex space. This is important information which enables us to derive the Gâteaux differentiability of the functional  $F_L$  at the set  $\mathcal{B}$  of ensemble  $v$ -representable densities. We will discuss this feature of  $F_L$  in the next section.

Having obtained some desirable convexity properties of  $F_L$  we try to obtain some analytic properties of this functional. An obvious question to ask is whether this functional is continuous. To be more precise, suppose that a series of densities  $n_k$  approaches a given density  $n$  in some sense, for instance  $\|n - n_k\|_1 \rightarrow 0$  and  $\|n - n_k\|_3 \rightarrow 0$  for  $k \rightarrow \infty$  in  $L^1 \cap L^3$ . Does this imply that  $|F_L[n_k] - F_L[n]| \rightarrow 0$ ? It turns out that this question is not easily answered. However, one can prove a weaker statement. Suppose  $n$  is an E-V-density corresponding to potential  $v$  of Hamiltonian  $\hat{H}_v$ . Then

$$\begin{aligned}
F_L[n] + \int d^3 r n(\mathbf{r}) v(\mathbf{r}) &= \text{Tr} \hat{D}[n] \hat{H}_v \leq \text{Tr} \hat{D}[n_k] \hat{H}_v \\
&= F_L[n_k] + \int d^3 r n_k(\mathbf{r}) v(\mathbf{r}) \quad (190)
\end{aligned}$$

and therefore

$$F_L[n] \leq F_L[n_k] + \int d^3 r v(\mathbf{r}) (n_k(\mathbf{r}) - n(\mathbf{r})) \quad (191)$$

Further, since  $n_k \rightarrow n$  in the norms on  $L^1 \cap L^3$  for each  $\epsilon > 0$  there is an integer  $M$  such that  $\|n - n_k\|_1 \leq \epsilon$  and  $\|n - n_k\|_3 \leq \epsilon$  for  $k > M$ . Now we can split up  $v \in L^{\frac{3}{2}} + L^\infty$  as  $v = u + w$  where  $u \in L^{\frac{3}{2}}$  and  $w \in L^\infty$  and we have

$$| \int d^3 r v(\mathbf{r}) (n_k(\mathbf{r}) - n(\mathbf{r})) | \leq \|u\|_{\frac{3}{2}} \|n - n_k\|_3 + \|w\|_\infty \|n - n_k\|_1 \quad (192)$$

So if  $\|n - n_k\|_1 \leq \epsilon/C$  and  $\|n - n_k\|_3 \leq \epsilon/C$ , where  $C = \|u\|_{\frac{3}{2}} + \|w\|_\infty$  then

$$F_L[n] \leq F_L[n_k] + \epsilon \quad (193)$$

for  $k$  sufficiently large. We therefore see that if we take  $\epsilon \rightarrow 0$  from above then  $F_L[n_k]$  approaches  $F_L[n]$  from above and  $n_k \rightarrow n$  in the norms on  $L^1 \cap L^3$ . This, of course, does not imply that  $F_L[n]$  is continuous in  $n$ . For that we would have to prove that  $|F_L[n] - F_L[n_k]| \leq \epsilon$  rather than  $F_L[n] - F_L[n_k] \leq \epsilon$ . What we have proven is a weaker form of continuity, known as semicontinuity. Because the limit point is a lower bound, the functional with the property in Eq.(193) is called lower semicontinuous. This can also be characterized differently. If we define  $\inf F[n_m]$  by  $\inf F_L[n_m] = \inf\{F_L[n_k] | k \geq m\}$  then lower semicontinuity implies

$$F_L[n] \leq \lim_{m \rightarrow \infty} \inf F_L[n_m] \quad (194)$$

Since we required that  $n$  is an E-V-density we have proven that  $F_L$  is lower semicontinuous on the set of E-V-densities. It turns out that one can prove that  $F_L$  is lower semicontinuous on all densities in  $\mathcal{S}$  (see theorem 4.4 of Lieb [1]). However, the proof of this is not simple and we will therefore not try to reproduce it here. Since the result is important we present it here in the form of a theorem

**Theorem 7** *Suppose  $n_k$  and  $n \in \mathcal{S}$  and  $n_k \rightarrow n$  for  $k \rightarrow \infty$  in the norms on  $L^1 \cap L^3$ . Then*

$$F_L[n] \leq \lim_{k \rightarrow \infty} \inf F_L[n_k]$$

*In other words  $F_L$  is lower semicontinuous on the set  $\mathcal{S}$ .*

One can prove an even stronger theorem in which we only need weak convergence of the series  $n_k$ . We will, however, not need that property in the remainder of this review. The notion of lower semicontinuity is an important property for convex functionals which will allow us to make several other useful statements about other properties of  $F_L$ . One particular consequence of lower semicontinuity that we will use, is that for a lower semicontinuous convex functional  $G : B \rightarrow \mathcal{R}$  the following set of points

$$\text{epi}(G) = \{(n, r) \in B \times \mathcal{R} | G[n] \leq r\} \quad (195)$$

is closed and convex [11]. This set is called the epigraph of  $G$  and is simply the set of points that lie above the graph of  $G$ . The closedness property means that if a series of points  $(n_k, r_k)$  in the epigraph of  $G$  converges to a point  $(n, r)$  then this point also lies in the epigraph. This also implies that the set of interior points of  $\text{epi}(G)$ , i.e. the set of points that lie strictly above  $G$ , is an open convex set (this means that for every point in this set there is a neighborhood that contains it). We will need this property in the next section.

### 13. Differentiability of $F_L$

In this section we will prove that the Lieb functional is differentiable on the set of E-V-densities and nowhere else. The functional derivative at a given E-V-density is equal to  $-v$  where  $v$  is the external potential that generates the E-V-density at which we take the derivative. To prove existence of the derivative we use the geometric idea that if a derivative of a functional  $G[n]$  in a point  $n_0$  exists, then there is a unique tangent line that touches the graph of  $G$  in a point  $(n_0, G[n_0])$ . To discuss this in more detail we have to define what we mean with a tangent. The discussion is simplified by the fact that we are dealing with convex functionals. If  $G : B \rightarrow \mathcal{R}$  is a differentiable and convex functional from a normed linear space  $B$  to the real numbers then from the convexity property it follows that for  $n_0, n_1 \in B$  and  $0 \leq \lambda \leq 1$  that

$$G[n_0 + \lambda(n_1 - n_0)] - G[n_0] \leq \lambda(G[n_1] - G[n_0]) \quad (196)$$

From the fact that  $G$  is differentiable we then find

$$G[n_1] - G[n_0] \geq \lim_{\lambda \rightarrow 0} \frac{G[n_0 + \lambda(n_1 - n_0)] - G[n_0]}{\lambda} = \frac{\delta G}{\delta n}[n_1 - n_0] \quad (197)$$

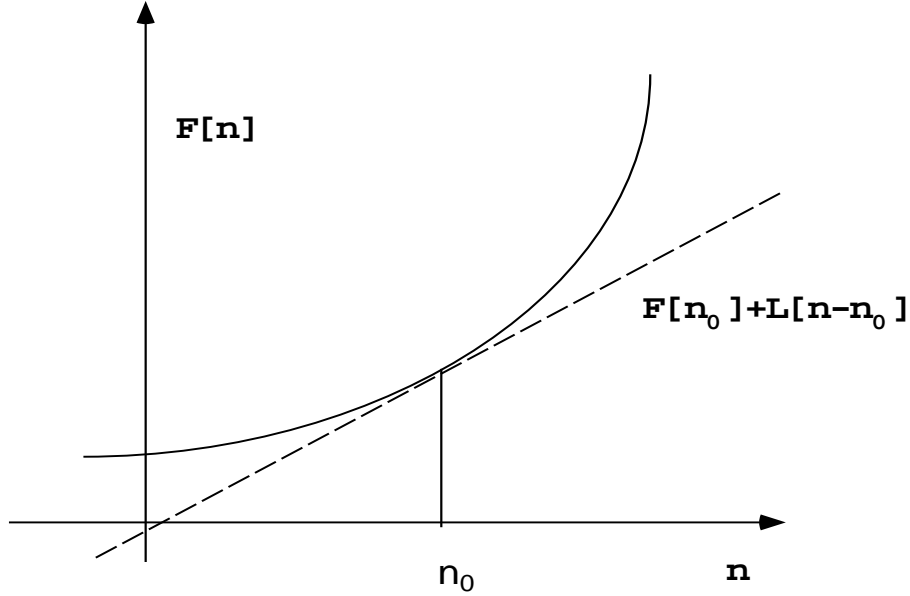
Therefore

$$G[n_1] \geq G[n_0] + \frac{\delta G}{\delta n}[n_1 - n_0] \quad (198)$$

Now  $\delta G/\delta n$  is a continuous linear functional which will be identified with a tangent. This is the basis of the following definition. If for a convex functional  $G$  there is a continuous linear functional  $L : B \rightarrow \mathcal{R}$  such that

$$G[n_1] \geq G[n_0] + L[n_1 - n_0] \quad (199)$$

then  $L$  is called a subgradient or tangent functional in  $n_0$ . The geometric idea behind this definition is illustrated in Figure 1.



**Figure 1: The convex functional  $F$  has a unique tangent functional  $L$  in the point  $n_0$**

For the Lieb functional  $F_L$  we will now prove the following statement:

**Theorem 8** *The functional  $F_L$  has a unique tangent functional for every E-V-density and nowhere else. Moreover the tangent functional at an E-V density  $n$  can be identified with  $-v$  where  $v$  is the potential that generates this density.*

In order to show this we first define the energy functional

$$E[v] = \inf_{\hat{D}} \text{Tr} \hat{D} \hat{H}_v \quad (200)$$

where the infimum is searched over all density matrices of the form given in Eq.(181). This is an extension of the previously defined functional in Eq.(130) to all potentials in  $L^{\frac{3}{2}} + L^\infty$ . One can further show that if an infimum exists the minimizing density matrix satisfies the Schrödinger equation [1]. Let us first suppose that  $n_0$  is an E-V-density corresponding

to potential  $v$  of Hamiltonian  $\hat{H}_v$ . Then

$$\begin{aligned} F_L[n_0] + \int d^3r n_0(\mathbf{r})v(\mathbf{r}) &= \text{Tr}\hat{D}[n_0]\hat{H}_v \leq \text{Tr}\hat{D}[n]\hat{H}_v \\ &= F_L[n] + \int d^3r n(\mathbf{r})v(\mathbf{r}) \end{aligned} \quad (201)$$

and therefore

$$F_L[n] \geq F_L[n_0] - \int d^3r v(\mathbf{r})(n(\mathbf{r}) - n_0(\mathbf{r})) \quad (202)$$

Therefore the functional  $L$

$$L[n] = - \int d^3r v(\mathbf{r})n(\mathbf{r}) \quad (203)$$

defines a linear and continuous functional (continuity follows from Eq.(192)) and is therefore a tangent functional. Now we have to show its uniqueness. Suppose  $L'$  is a different tangent functional. Since  $F$  is defined on  $B = L^1 \cap L^3$  the tangent functional must represent an element in the dual space  $B^* = L^{\frac{3}{2}} + L^\infty$  and can be written as

$$L'[n] = - \int d^3r \tilde{v}(\mathbf{r})n(\mathbf{r}) \quad (204)$$

with  $\tilde{v} \in L^{\frac{3}{2}} + L^\infty$  and  $\tilde{v} \neq v + C$ . Now since we assumed that  $L'$  was also tangent functional we have

$$F_L[n] \geq F_L[n_0] - \int d^3r \tilde{v}(\mathbf{r})(n(\mathbf{r}) - n_0(\mathbf{r})) \quad (205)$$

and hence

$$F_L[n] + \int d^3r n(\mathbf{r})\tilde{v}(\mathbf{r}) \geq F_L[n_0] + \int d^3r n_0(\mathbf{r})\tilde{v}(\mathbf{r}) \quad (206)$$

We take the infimum over all densities in  $\mathcal{S}$  on the left hand side. Since we know that there is ground state density matrix corresponding to  $n_0$  we obtain from Eq.(206):

$$E[\tilde{v}] = \inf_{n \in \mathcal{S}} \{F_L[n] + \int d^3r n(\mathbf{r})\tilde{v}(\mathbf{r})\} \geq \text{Tr}\hat{D}[n_0]\hat{H}_{\tilde{v}} \quad (207)$$

Now there are two cases, either the Hamiltonian with potential  $\tilde{v}$  is able to support a bound ground state or it is not. If it does support a ground state then

$$\text{Tr}\hat{D}[n_0]\hat{H}_{\tilde{v}} > E[\tilde{v}] \quad (208)$$

since  $\hat{D}[n_0]$  is not a ground state density matrix for  $\tilde{v}$ . Together with Eq.(207) this immediately leads to the contradiction  $E[\tilde{v}] > E[\tilde{v}]$ . If the Hamiltonian with potential  $\tilde{v}$  does not support a bound ground state then there is no normalized density matrix for which the infimum of  $E[\tilde{v}]$  as in Eq.(200) is attained. We then again obtain Eq.(208) and the same contradiction  $E[\tilde{v}] > E[\tilde{v}]$ . We therefore conclude that the E-V-density  $n_0$  has a unique tangent functional equal to  $-v$  where  $v$  is the potential that yields ground state density  $n_0$ .

Let us now suppose that  $n_0$  is not an E-V-density. Let us further suppose that there is a tangent functional at  $n_0$ , i.e. that for some  $\tilde{v}$  Eq. (205) and therefore also Eq.(206) are satisfied. The constrained search for  $F_L[n_0]$  always has a minimizing density matrix, which we call  $\hat{D}[n_0]$ . With this density matrix then also Eq.(207) is true. Since  $n_0$  is not an E-V-density  $\hat{D}[n_0]$  can not be a ground state density matrix for the Hamiltonian with potential  $\tilde{v}$ . With the same arguments as before we find that Eq.(208) must be true which again leads to the contradiction  $E[\tilde{v}] > E[\tilde{v}]$ . Therefore there is no tangent functional at  $n_0$  if  $n_0$  is not an E-V-density. We have therefore proven our statement, there is a unique tangent functional at every E-V-density and nowhere else.

As a next step we will show that this implies that the functional  $F_L$  Gâteaux differentiable at every E-V-density and nowhere else. For the application of the next theorem it is desirable to extend the domain of  $F_L$  to all of  $L^1 \cap L^3$ . We follow Lieb [1] and define

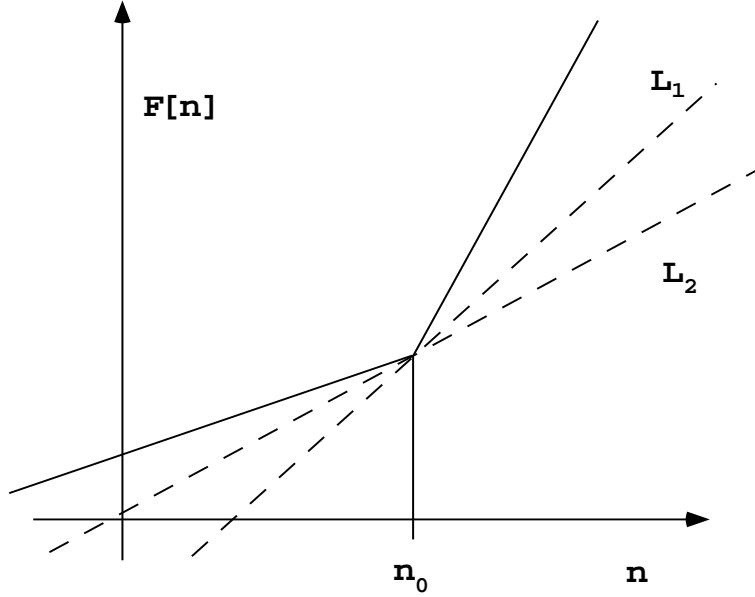
$$F_L[n] = \begin{cases} \inf_{\hat{D} \rightarrow n} \text{Tr} \hat{D}(\hat{T} + \hat{W}) & \text{if } n \in \mathcal{S} \\ +\infty & \text{if } n \in L^1 \cap L^3 \text{ and } n \notin \mathcal{S} \end{cases} \quad (209)$$

The reader may seem surprised with the appearance of  $+\infty$  in this definition. However, infinite values are well-defined in the theory of convex functionals [11] and they are usually introduced to deal in a simple way with domain questions. With this definition the functional  $F_L$  is a convex lower semicontinuous functional of the whole space  $L^1 \cap L^3$ . We are now ready to introduce the following key theorem which we will use to prove differentiability of  $F_L$  at the set of E-V-densities:

**Theorem 9** *Suppose  $F : B \rightarrow \mathcal{R}$  is a lower semicontinuous convex functional which is finite at a convex subset  $V \subset B$  of a normed linear space  $B$ . If  $F$  has a unique continuous tangent functional  $L : B \rightarrow \mathcal{R}$  at  $n_0 \in V$  then  $F$  is Gâteaux differentiable at  $n_0$  and  $L = \delta F / \delta n$ .*

The fact that uniqueness of a tangent functional implies differentiability is clear from a geometric point of view. In Figure 2 we display an example of a functional (in this picture the functional is simply a function) which is not differentiable at  $n_0$ . Consequently, there is no unique tangent functional

at that point. In the example there are in fact infinitely many tangent functionals at  $n_0$  of which there are two drawn in the plot.



**Figure 2: The convex functional  $F$  has no unique tangent functional in the point  $n_0$ . Both  $L_1$  and  $L_2$  are tangent functionals**

In the case of infinitely many dimensions one should, however, be careful in drawing conclusions from simple plots and we have to resort to formal proofs. Since the proof of the previous theorem is important for our discussion and not difficult to follow we will present it here. Since  $V$  is a convex set we have that if  $n_0 \in V$  and  $n_1 \in V$  then  $n_0 + \lambda(n_1 - n_0) \in V$  for  $0 \leq \lambda \leq 1$  and since  $F$  is convex we obtain

$$F[n_0 + \lambda(n_1 - n_0)] \leq F[n_0] + \lambda(F[n_1] - F[n_0]) \quad (210)$$

Furthermore since  $F$  has a unique continuous tangent functional at  $n_0$  we have

$$F[n_0 + \lambda(n_1 - n_0)] \geq F[n_0] + \lambda L[n_1 - n_0] \quad (211)$$

Note that  $n_1 - n_0$  need not be in  $V$  but is always in  $B$  since that is a linear space. If we combine the two inequalities we find that

$$F[n_1] - F[n_0] \geq \frac{F[n_0 + \lambda(n_1 - n_0)] - F[n_0]}{\lambda} \geq L[n_1 - n_0] \quad (212)$$

Now since  $F$  is convex the function  $g(\lambda) = F[n_0 + \lambda(n_1 - n_0)] - F[n_0]$  is a convex real function on the interval  $[0, 1]$  and hence continuous. Moreover, as the equation above shows, the function  $g(\lambda)/\lambda$  has a finite upper and lower bound and therefore the limit  $\lambda \rightarrow 0$  of  $g(\lambda)/\lambda$  exists. We therefore find

$$F[n_1] - F[n_0] \geq F'[n_0, n_1] \geq L[n_1 - n_0] \quad (213)$$

where

$$F'[n_0, n_1] = \lim_{\lambda \rightarrow 0} \frac{F[n_0 + \lambda(n_1 - n_0)] - F[n_0]}{\lambda} \quad (214)$$

It remains to show that  $F'[n_0, n_1]$  is continuous and linear and equal to  $L$ . Now  $F'$  has the property that for  $n_2 \in V$

$$F'[n_0, n_0 + \epsilon(n_2 - n_0)] = \lim_{\lambda \rightarrow 0} \frac{F[n_0 + \lambda\epsilon(n_2 - n_0)] - F[n_0]}{\lambda} = \epsilon F'[n_0, n_2] \quad (215)$$

Therefore from Eq.( 213) we find

$$F[n_0 + \epsilon(n_1 - n_0)] \geq F[n_0] + \epsilon F'[n_0, n_1] \quad (216)$$

This means that the straight line

$$\mathcal{L} = \{(n_0 + \epsilon(n_1 - n_0), F[n_0] + \epsilon F'[n_0, n_1]) \in B \times \mathcal{R} | \epsilon \in [0, 1]\} \quad (217)$$

lies below the graph of functional  $F$ . Now since  $F$  is convex and lower semicontinuous the set of points above the graph of  $F$  (the interior points of  $\text{epi}(F)$ ) form an open convex set which is nonempty since  $F$  is finite on  $V$  [11]. Now a famous theorem of functional analysis, the Hahn-Banach theorem, tells us that if we have an open convex set  $A$  (the interior of  $\text{epi}(F)$  in our case) and an affine subspace  $\mathcal{L}$  (which is the line  $\mathcal{L}$  in our case) that does not intersect  $A$  then there is a hyperplane  $\mathcal{H}$  that contains  $\mathcal{L}$  in which the hyperplane  $\mathcal{H}$  has the form

$$\mathcal{H} = \{(n, r) \in B \times \mathcal{R} | L'[n] + \alpha r = \beta\} \quad (218)$$

where  $L' : B \rightarrow \mathcal{R}$  is a continuous linear functional and  $\alpha$  and  $\beta$  are real numbers (We can take  $\alpha \neq 0$  since  $F'[n_0, n_1]$  is finite and we will have no vertical line  $\mathcal{L}$  or vertical hyperplane  $\mathcal{H}$ ). We will not prove the Hahn-Banach theorem as it is geometrically intuitive and can be found in most textbooks on functional analysis [20, 21]. We will just use its consequences.



Now we know that our line  $\mathcal{L}$  is contained in  $\mathcal{H}$ . The coefficient  $\beta$  is then determined by the fact that  $(n_0, F[n_0]) \in \mathcal{H}$  and we find  $\beta = L'[n_0] + \alpha F[n_0]$  and therefore

$$\mathcal{H} = \{(n, r) \in B \times \mathcal{R} | L'[n - n_0] + \alpha(r - F[n_0]) = 0\} \quad (219)$$

Now from the fact that  $(n_0 + \epsilon(n_1 - n_0), F[n_0] + \epsilon F'[n_0, n_1]) \in \mathcal{H}$  we find that

$$L'[n_1 - n_0] + \alpha F'[n_0, n_1] = 0 \quad (220)$$

From this equation and Eq.(213) we then see immediately that  $-L'/\alpha$  is a continuous tangent functional at  $n_0$  which then must be equal to  $L$  since that was the only continuous tangent functional at  $n_0$ . Consequently

$$F'[n_0, n_1] = L[n_1 - n_0] \quad (221)$$

and thus

$$\frac{\delta F}{\delta n}[n_1 - n_0] = \lim_{\lambda \rightarrow 0} \frac{F[n_0 + \lambda(n_1 - n_0)] - F[n_0]}{\lambda} = L[n_1 - n_0] \quad (222)$$

We therefore obtained what we wanted to prove,  $F$  is Gâteaux differentiable at  $n_0$  and  $\delta F/\delta n = L$ . Now we can apply this theorem to the Lieb functional. If we take  $F = F_L$ ,  $B = L^1 \cap L^3$ ,  $V = \mathcal{S}$  and use that  $F_L$  has a unique tangent functional  $L = -v$  at every E-V-density and nowhere else, we obtain:

**Theorem 10** *The functional  $F_L$  is Gâteaux differentiable for every E-V-density in the set  $\mathcal{S}$  and nowhere else. Moreover the functional derivative at an E-V-density is equal to  $-v$  where  $v$  is the potential that generates this density.*

This leaves us with the question which densities in set  $\mathcal{S}$  actually are E-V-densities. A useful result on this point is obtained in the next section.

## 14. Ensemble $v$ -representability

We have seen that the Lieb functional  $F_L$  is differentiable at the set of E-V-densities in  $\mathcal{S}$  and nowhere else. For this reason it is desirable to know a bit more about these densities. The question therefore is: which densities are ensemble  $v$ -representable? In this section we will prove a useful result which will enable us to put the Kohn-Sham approach on a rigorous basis.

**Theorem 11** *The set of E-V-densities is dense in the set  $\mathcal{S}$  with respect to the norm on  $L^1 \cap L^3$ .*

This statement means the following. Suppose we take an arbitrary density  $n_0$  from the set  $\mathcal{S}$ , then for every  $\epsilon > 0$  we can find an E-V-density  $n$  such that  $\|n_0 - n\|_1 \leq \epsilon$  and  $\|n_0 - n\|_3 \leq \epsilon$ . In other words, for every density in the set  $\mathcal{S}$  there is an E-V-density arbitrarily close to it. This can also be phrased differently. For every density  $n_0$  in the set  $\mathcal{S}$  there is a series of E-V-densities  $n_k$  such that

$$\lim_{k \rightarrow \infty} \|n_0 - n_k\|_p = 0 \quad (223)$$

where the subindex for the norm takes the values  $p = 1$  and  $p = 3$ . In order to establish this result we need to use a theorem due to Bishop and Phelps. For the clarity of the discussion we split the theorem into two parts which both yield interesting results for our functional  $F_L$ . The first part gives some insight in the set of potentials  $\mathcal{V}$  that generate a bound ground state. From the relation

$$E[v] = \inf_{n \in \mathcal{S}} \{F_L[n] + \int d^3r n(\mathbf{r})v(\mathbf{r})\} \quad (224)$$

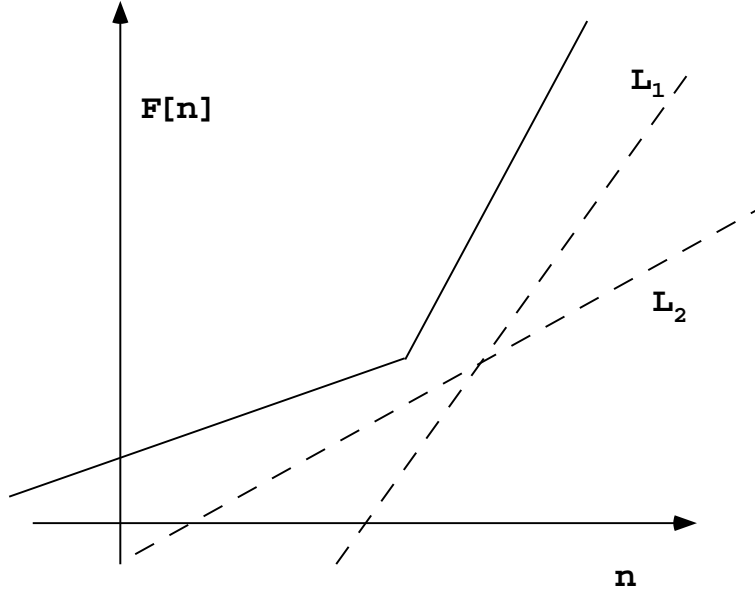
we obtain immediately that for any  $n \in \mathcal{S}$  and any  $v \in L^{\frac{3}{2}} + L^\infty$

$$F_L[n] \geq - \int d^3r n(\mathbf{r})v(\mathbf{r}) + E[v] \quad (225)$$

Now the functional on the right hand side of the inequality sign is, for a given  $v$ , a linear functional of  $n$ . The inequality sign tells us that this functional lies below the graph of  $F_L[n]$ . A linear functional with this property is called  $F_L$ -bounded. Let us give a general definition of these linear functionals. Let  $F$  be a functional  $F : B \rightarrow \mathcal{R}$  from a normed function space (a Banach space)  $B$  to the real numbers. Let  $B^*$  be the dual space of  $B$ , i.e. the set of continuous linear functionals on  $B$ . Then  $L \in B^*$  is said to be  $F$ -bounded if there is a constant  $C$  such that for all  $n \in B$

$$F[n] \geq L[n] + C \quad (226)$$

where the constant  $C$  may depend on  $L$  but not on  $n$ . We therefore see from Eq.(225) that every  $v \in L^{\frac{3}{2}} + L^\infty$  defines an  $F_L$ -bounded functional where  $L$  is defined as in Eq.(203). The geometric picture of an  $F$ -bounded functional is displayed in Figure 3.



**Figure 3:** Both  $L_1$  and  $L_2$  are  $F$ -bounded by the convex functional  $F$

Note that the tangent functionals of  $F_L$  are special cases of  $F_L$ -bounded functionals, they are the  $F_L$  bounded functionals that also touch the graph of  $F_L$ . Therefore the set of tangent functionals is a subset of the set of  $F_L$ -bounded functionals. This can be illustrated with an example. Consider the function  $f(x) = \exp(x)$  on the real axis. This function is convex and all tangent functions are of the form  $g_\alpha(x) = \alpha x + \beta$  where  $\alpha > 0$  and  $\beta(\alpha) \leq 1$ . The constant function  $g_0(x) = \beta$  with  $\beta \leq 0$  is an  $f$ -bounded function, but not a tangent. However, we can always find a tangent with a slope arbitrary close to zero, i.e. arbitrary close to the slope of the constant  $f$ -bounded function  $g_0$ . The following theorem (due to Bishop and Phelps) ensures that a similar situation occurs for the case of general Banach spaces:

**Theorem 12 (Bishop-Phelps I)** *Let  $F : B \rightarrow \mathcal{R}$  be a lower semicontinuous convex functional on a real Banach space  $B$ . The functional  $F$  can take the value  $+\infty$  but not everywhere. Then the continuous tangent functionals to  $F$  are  $B^*$ -norm dense in the set of  $F$ -bounded functionals in  $B^*$ .*

This means that if  $L_0$  is some  $F$ -bounded functional then we can find a set of tangent functionals  $L_k$  such that

$$\lim_{k \rightarrow \infty} \|L_0 - L_k\|_{B^*} = 0 \quad (227)$$

where the limit is taken in the norm on  $B^*$ . We will not prove this theorem here. The proof is clearly described with a geometric interpretation in reference [22]. Let us apply this theorem to our functional  $F_L$ . We know that every tangent functional of  $F_L$  can be identified with  $-v$ , where  $v$  is a potential that yields a bound ground state, i.e.  $v \in \mathcal{V}$ . Now we know that every element  $-v_0$  for an arbitrary  $v_0 \in L^{\frac{3}{2}} + L^\infty$  corresponds to an  $F_L$ -bounded functional. Therefore for such a  $v_0$  there is a series of  $v_k \in \mathcal{V}$  such that

$$\lim_{k \rightarrow \infty} \|v_0 - v_k\| = 0 \quad (228)$$

where the norm is the  $L^{\frac{3}{2}} + L^\infty$ -norm described in Eq.(24). Therefore every potential  $v_0 \in L^{\frac{3}{2}} + L^\infty$  can be approximated to arbitrary accuracy by a potential that yields a bound ground state. This may seem counterintuitive at first sight as one can imagine  $v_0$  to be a repulsive potential, until one realizes that one may put the system in big box with a wall of finite height. This system will have a bound state if the size of the box is chosen to be big enough. The particles will then spread out over the box in order to minimize the repulsion between them. If we choose  $v_k = v_0 + w_k$  where  $w_k$  describes a series of boxes of increasing size but with decreasing height of the potential wall then we see that we have created a series of potentials in  $\mathcal{V}$  that approaches  $v_0$  to an arbitrary accuracy. Let us now discuss the second part of the Bishop-Phelps theorem

**Theorem 13 (Bishop-Phelps II)** *Let  $F : B \rightarrow \mathcal{R}$  be a lower semicontinuous convex functional on a real Banach space  $B$ . The functional  $F$  can take the value  $+\infty$  but not everywhere. Suppose  $n_0 \in B$  with  $F[n_0] < \infty$  and let  $L_0 \in B^*$  be an  $F$ -bounded functional. Then for every  $\epsilon \geq 0$  there exists  $n_\epsilon \in B$  and a functional  $L_\epsilon \in B^*$  such that*

1.  $\|L_\epsilon - L_0\|_{B^*} \leq \epsilon$
2.  $F[n] \geq F[n_\epsilon] + L_\epsilon[n - n_\epsilon]$  for all  $n$ .
3.  $\epsilon \|n_\epsilon - n_0\|_B \leq F[n_0] - L_0[n_0] - \inf_{n \in B} \{F[n] - L_0[n]\}$

For the details of the proof we again refer to [22]. The first two points of this theorem are equivalent to the previous theorem. They say that any  $F$ -bounded functional  $L_0$  can be approximated to arbitrary accuracy by a tangent functional  $L_\epsilon$ . The inequality in the third point of this theorem

allows us to make statements about distances between elements in  $B$ , which in our case will be densities. Note that the right hand side of this inequality has the geometric meaning of being the difference of the vertical distance of the functionals  $L_0$  and  $F$  in  $n_0$  and the shortest possible distance between  $L_0$  and  $F$ . Let us now apply this theorem to the functional  $F_L$  and show that every density in  $\mathcal{S}$  is arbitrarily close to an E-V-density. We first need some preliminaries. From Eq.(224) we see that we can write

$$F_L[n] = \sup_{v \in L^{\frac{3}{2}} + L^\infty} \{E[v] - \int d^3r n(\mathbf{r})v(\mathbf{r})\} \quad (229)$$

If the supremum is attained for some  $v$  then  $n$  is an E-V-density. This follows because then there is a density matrix  $\hat{D}[n]$  that yields density  $n$  (see Theorem 5) such that

$$\text{Tr} \hat{D}[n] \hat{H}_v = F_L[n] + \int d^3r n(\mathbf{r})v(\mathbf{r}) = E[v] = \inf_{\hat{D}} \text{Tr} \hat{D} \hat{H}_v \quad (230)$$

The density matrix  $\hat{D}[n]$  must therefore be a ground state density matrix. If  $n$  is not an E-V-density then the supremum is not attained for any  $v$ . In any case, for every integer  $k$  and any density  $n_0 \in \mathcal{S}$  we can always find some  $v_k$  such that

$$\begin{aligned} E[v_k] - \int d^3r n_0(\mathbf{r})v_k(\mathbf{r}) &\geq \sup_{v \in L^{\frac{3}{2}} + L^\infty} \{E[v] - \int d^3r n_0(\mathbf{r})v(\mathbf{r})\} - \frac{1}{k} \\ &= F_L[n_0] - \frac{1}{k} \end{aligned} \quad (231)$$

where we note that the series  $v_k$  does not converge to any  $v$  if  $n_0$  is not an E-V-density. Furthermore, for any  $n$  we have

$$E[v_k] = \inf_{n \in \mathcal{S}} \{F_L[n] + \int d^3r n(\mathbf{r})v_k(\mathbf{r})\} \leq F_L[n] + \int d^3r n(\mathbf{r})v_k(\mathbf{r}) \quad (232)$$

which in combination with the previous inequality yields

$$F_L[n] + \int d^3r n(\mathbf{r})v_k(\mathbf{r}) \geq E[v_k] \geq F_L[n_0] + \int d^3r n_0(\mathbf{r})v_k(\mathbf{r}) - \frac{1}{k} \quad (233)$$

We are now ready to apply the Bishop-Phelps theorem to the Lieb functional  $F_L$ . We take  $\epsilon = 1$ ,  $n_0 \in \mathcal{S}$  and let  $-v_k$  correspond to the  $F$ -bounded functional  $L_0$  of the theorem. According to the theorem we can then find a tangent functional  $-w_k$  (the  $L_\epsilon$  of the theorem) such that

$$\|v_k - w_k\| \leq 1 \quad (234)$$

in the norm on  $L^{\frac{3}{2}} + L^\infty$ . From our previous investigations we know that the tangent  $-w_k$  touches the graph of  $F_L$  in an E-V-density  $n_k$ , i.e.

$$F_L[n] \geq F_L[n_k] - \int d^3r w_k(\mathbf{r})(n(\mathbf{r}) - n_k(\mathbf{r})) \quad (235)$$

where  $w_k$  is the potential that generates density  $n_k$ . The Bishop-Phelps theorem then tells us that

$$\begin{aligned} \|n_k - n_0\|_p &\leq F_L[n_0] + \int d^3r n_0(\mathbf{r})v_k(\mathbf{r}) \\ &- \inf_{n \in \mathcal{S}} \{F_L[n] + \int d^3r n(\mathbf{r})v_k(\mathbf{r})\} \end{aligned} \quad (236)$$

where the normindex has the values  $p = 1$  and  $p = 3$ . Note that the infimum in this equation can be taken over  $\mathcal{S}$  rather than  $L^1 \cap L^3$  since  $F_L$  is defined to be  $+\infty$  outside  $\mathcal{S}$ . Then from Eq.(233) we see immediately that

$$\inf_{n \in \mathcal{S}} \{F_L[n] + \int d^3r n(\mathbf{r})v_k(\mathbf{r})\} \geq F_L[n_0] + \int d^3r n_0(\mathbf{r})v_k(\mathbf{r}) - \frac{1}{k} \quad (237)$$

and therefore

$$\|n_k - n_0\|_p \leq \frac{1}{k} \quad (238)$$

for  $p = 1$  and  $p = 3$ . Since this equation is true for any  $k$  we see that any density  $n_0 \in \mathcal{S}$  can be approximated to any accuracy by the E-V-density  $n_k$  in the norms on  $L^1 \cap L^3$ . This proves the theorem in the beginning of this section.

## 15. The Kohn-Sham approach and noninteracting $v$ -representability

We have now come to the discussion of the central equations which form the basis of almost any practical application of density functional theory: the Kohn-Sham equations. Kohn and Sham [8] introduced an auxiliary noninteracting system of particles with the property that it yields the same ground state density as the real interacting system. In order to put the Kohn-Sham procedure on a rigorous basis we introduce the functional

$$T_L[n] = \inf_{\hat{D} \rightarrow n} \text{Tr} \hat{D} \hat{T} \quad (239)$$

We see that this is simply the Lieb functional with the two-particle interaction omitted. All the properties of the functional  $F_L$  carry directly over to  $T_L$ . The reason is that all these properties were derived on the basis

of the variational principle in which we only required that  $\hat{T} + \hat{W}$  is an operator that is bounded from below. This is, however, still true if we omit the Coulomb repulsion  $\hat{W}$ . We therefore conclude that  $T_L$  is a convex lower semicontinuous functional which is differentiable for any density  $n$  that is ensemble  $v$ -representable for the noninteracting system and nowhere else. We refer to such densities as noninteracting E-V-densities and denote the set of all noninteracting E-V-densities by  $\mathcal{B}_0$ . Let us collect all the results for  $T_L$  in a single theorem:

**Theorem 14**  *$T_L$  is a convex lower semicontinuous functional with the following properties:*

1. *For any  $n \in \mathcal{S}$  there is a minimizing density matrix  $\hat{D}[n]$  with the property  $T_L[n] = \text{Tr} \hat{D}[n] \hat{T}$ .*
2.  *$T_L$  is Gâteaux differentiable at the set of noninteracting E-V-densities and nowhere else.*
3. *The functional derivative at a noninteracting E-V-density  $n$  is given by:*

$$\frac{\delta T_L}{\delta n(\mathbf{r})} = -v_s[n](\mathbf{r})$$

*where the potential  $v_s$  generates the density  $n$  in a noninteracting system.*

From the last point in this theorem we see that if we want to know if a given density  $n$  from the set  $\mathcal{S}$  can be obtained as an E-V-density of a noninteracting system we may try to calculate the derivative of  $T_L$  for this density. If it exists then the derivative yields the potential that we were looking for. Now Kohn and Sham [8] assumed that for any density of an interacting system there is a noninteracting system that has the same density as its ground state. We can now ask the question whether the sets of interacting and noninteracting E-V-densities are equal. This is currently not known. However, we can make a number of useful conclusions. First of all, if we apply the Bishop-Phelps theorem to the functional  $T_L$  we obtain the following result:

**Theorem 15** *The set of noninteracting E-V-densities is dense in the set  $\mathcal{S}$  with respect to the norm on  $L^1 \cap L^3$ .*

This means that for any density  $n \in \mathcal{S}$  there is a noninteracting E-V-density arbitrarily close. We can in particular choose  $n$  to be an interacting E-V-density, i.e.  $n \in \mathcal{B}$  and find a noninteracting E-V-density arbitrarily close. We also know from the Bishop-Phelps theorem applied to  $F_L$  that the set of interacting E-V-densities is dense in  $\mathcal{S}$  and therefore for any  $n \in \mathcal{S}$ , in

particular  $n \in \mathcal{B}_0$ , we can find an interacting E-V-density arbitrarily close. We therefore conclude

**Theorem 16** *The set  $\mathcal{B}_0$  of noninteracting E-V-densities is dense in the set  $\mathcal{B}$  of interacting E-V-densities, and vice versa.*

If we combine this result with previous theorems we obtain the following important consequence for the Kohn-Sham scheme:

**Theorem 17** *Suppose  $n \in \mathcal{B}$  is an interacting E-V-density. Then for every  $\epsilon > 0$  there is a noninteracting E-V-density  $n_\epsilon \in \mathcal{B}_0$  such that*

1.  $\|n - n_\epsilon\|_p \leq \epsilon$  for  $p = 1$  and  $p = 3$ .
2. *The density  $n_\epsilon$  is a ground state ensemble density of a noninteracting system with potential*

$$v_{s,\epsilon}(\mathbf{r}) = -\frac{\delta T_L}{\delta n(\mathbf{r})}(n_\epsilon)$$

*i.e. we can always set up a Kohn-Sham scheme that produces a given interacting E-V-density to arbitrary accuracy.*

This theorem tells us that in practice we can always set up a Kohn-Sham scheme. We also see that if we want to prove that the sets  $\mathcal{B}$  and  $\mathcal{B}_0$  of interacting and noninteracting E-V-densities are equal, then we have to show that the potentials  $v_{s,\epsilon}$  in this theorem approach some potential  $v_{s,0}$  for  $\epsilon \rightarrow 0$  in some smooth way. This, however, has not been proven until now. In numerical calculations (see the discussion at the end of this section) one has indeed always succeeded in obtaining a Kohn-Sham potential for given interacting E-V-densities obtained from accurate Configuration Interaction (CI) calculations. In these calculations convergence to a given Kohn-Sham potential is sometimes difficult to obtain, but seems to happen in a rather smooth way. One might therefore expect that the sets of interacting and noninteracting E-V-densities are in fact equal. In order to encourage further work in this field we put it here as a conjecture

**Conjecture 1** *The sets  $\mathcal{B}$  and  $\mathcal{B}_0$  of interacting and noninteracting E-V-densities are equal, i.e.  $\mathcal{B} = \mathcal{B}_0$ .*

Let us describe a couple of cases for which we know this conjecture to be true. Consider a system of two particles. Let the interacting system have density  $n$ . Then we can construct a noninteracting Kohn-Sham system with ground state wavefunction

$$\Psi_{KS}(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2) = \frac{1}{\sqrt{2}}\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)(\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)) \quad (240)$$



where  $\alpha$  and  $\beta$  are the usual spin functions with  $\alpha(\frac{1}{2}) = \beta(-\frac{1}{2}) = 1$  and  $\alpha(-\frac{1}{2}) = \beta(\frac{1}{2}) = 0$ . This wavefunction has a density  $n(\mathbf{r}) = 2|\varphi(\mathbf{r})|^2$  and the Kohn-Sham orbital  $\varphi$  satisfies

$$\left(-\frac{1}{2}\nabla^2 + v_s[n](\mathbf{r})\right)\varphi(\mathbf{r}) = \epsilon\varphi(\mathbf{r}) \quad (241)$$

If we now choose  $\varphi(\mathbf{r}) = \sqrt{\varphi(\mathbf{r})/2}$  then for an interacting E-V-density  $n$  the Kohn-Sham Hamiltonian with potential

$$v_s[n](\mathbf{r}) = \frac{1}{2} \frac{\nabla^2 \sqrt{n}}{\sqrt{n}} + \epsilon \quad (242)$$

has orbital  $\varphi$  as an eigenfunction. Because the density is positive the orbital  $\varphi = \sqrt{n/2}$  has no nodes and must be a ground state orbital. We therefore have constructed a noninteracting system with ground state  $n$ , which is even a pure state density.

Another case where the conjecture is true is for lattice systems. The lattice system is obtained by discretizing the many-body Hamiltonian on a grid, i.e. we replace the differential equation by a difference equation as one might do to solve the Schrödinger equation numerically. Then any interacting E-V-density on the grid is also a noninteracting E-V-density. This was proven by Chayes, Chayes and Ruskai [23]. This work may be used to prove the general conjecture above if one can prove that the continuum limit can be taken in some smooth way.

Let us finally discuss the exchange-correlation functional which is the central object in any application of density functional theory. We define the exchange-correlation functional  $E_{xc}$  by

$$F_L[n] = T_L[n] + \frac{1}{2} \int d^3r_1 d^3r_2 \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + E_{xc}[n] \quad (243)$$

Since both  $T_L$  and  $F_L$  are defined on the set  $\mathcal{S}$  the exchange-correlation functional  $E_{xc}$  is also defined on that set. Since  $F_L$  and  $T_L$  are differentiable respectively on the sets  $\mathcal{B}$  and  $\mathcal{B}_0$  and nowhere else, the functional  $E_{xc}$  is differentiable on  $\mathcal{B} \cap \mathcal{B}_0$  and nowhere else. The derivative of Eq.(243) on that set is given by

$$-v(\mathbf{r}) = -v_s(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \quad (244)$$

If we define the exchange-correlation potential by

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \quad (245)$$

then we see that the Kohn-Sham potential can be written as

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}) \quad (246)$$

We see that on the set  $\mathcal{B} \cap \mathcal{B}_0$  we have obtained the usual Kohn-Sham equations

$$\left[ \hat{T} + \hat{V} + \hat{V}_H[n] + \hat{V}_{xc}[n] \right] |\Phi_i\rangle = E_0 |\Phi_i\rangle \quad (247)$$

where  $i = 1 \dots q$  runs over the  $q$  degenerate ground states  $|\Phi_i\rangle$  of the Kohn-Sham system. The density must now be calculated from a ground state ensemble

$$\hat{D}_s[n] = \sum_{i=1}^q \mu_i |\Phi_i\rangle \langle \Phi_i| \quad (248)$$

of the Kohn-Sham system and is explicitly given as

$$n(\mathbf{r}) = \text{Tr} \hat{D}_s[n] \hat{n}(\mathbf{r}) = \sum_{i=1}^q \mu_i \langle \Phi_i | \hat{n}(\mathbf{r}) | \Phi_i \rangle \quad (249)$$

These equations can be written more explicitly in terms of the Kohn-Sham orbitals defined to be the eigenstates of the single particle equation

$$\left( -\frac{1}{2} \nabla^2 + v_s(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad (250)$$

It is then easily seen that any Slater determinant

$$|\Phi\rangle = |\varphi_{i_1} \dots \varphi_{i_N}\rangle \quad (251)$$

built out of Kohn-Sham orbitals is an eigenstate of the Kohn-Sham system with eigenvalue  $E_0 = \epsilon_{i_1} + \dots + \epsilon_{i_N}$ . However, not every eigenstate is necessarily a Slater determinant. For instance, if two Slater determinants have the same energy eigenvalue, then a linear combination of them also has the same eigenvalue. This leads to a subtle point for Kohn-Sham theory of degenerate states. In Eq.(249) we require that the density is representable by a ground state ensemble of a noninteracting system. However, we did not require that it must be representable by an ensemble of ground state Slater determinants. That one should be careful at this point, has been shown by Englisch and Englisch [3] and Lieb [1]. They constructed an explicit example of a pure state density of a noninteracting system that can not be obtained from a single Slater determinant. We will therefore in general have

$$|\Phi_i\rangle = \sum_{j=1}^q \alpha_{ij} |D_j\rangle \quad (252)$$

were  $|D_j\rangle$  is a Slater determinant. We further know that every  $|\Phi_i\rangle$  must be a ground state for potential  $v_s$ . This means that all orbitals below the highest occupied level must be occupied. If this were not the case then we could lower the energy by transferring an electron from the highest level to a lower level which would lower the energy and therefore  $|\Phi_i\rangle$  would not be a ground state for potential  $v_s$ . This also means that if two determinants  $|D_i\rangle$  and  $|D_j\rangle$  differ, then this difference must be due to different orbitals in the highest level. Because both determinants are eigenfunctions of the Kohn-Sham Hamiltonian it is easily seen that these different orbitals must have the same Kohn-Sham eigenvalue. This eigenvalue is the Kohn-Sham orbital energy of the highest occupied state which we will denote by  $\mu$ . From these considerations we find that the density is of the general form

$$n(\mathbf{r}) = \sum_{\epsilon_i < \mu} |\varphi_i(\mathbf{r})|^2 + \sum_{\epsilon_k = \epsilon_l = \mu} \beta_{kl} \varphi_k(\mathbf{r}) \varphi_l^*(\mathbf{r}) \quad (253)$$

where  $\beta_{kl}$  is an Hermitian matrix with eigenvalues between 0 and 1. This means that we can diagonalize this matrix with a unitary matrix  $U_{ij}$ . We then introduce new orbitals for the highest occupied level:

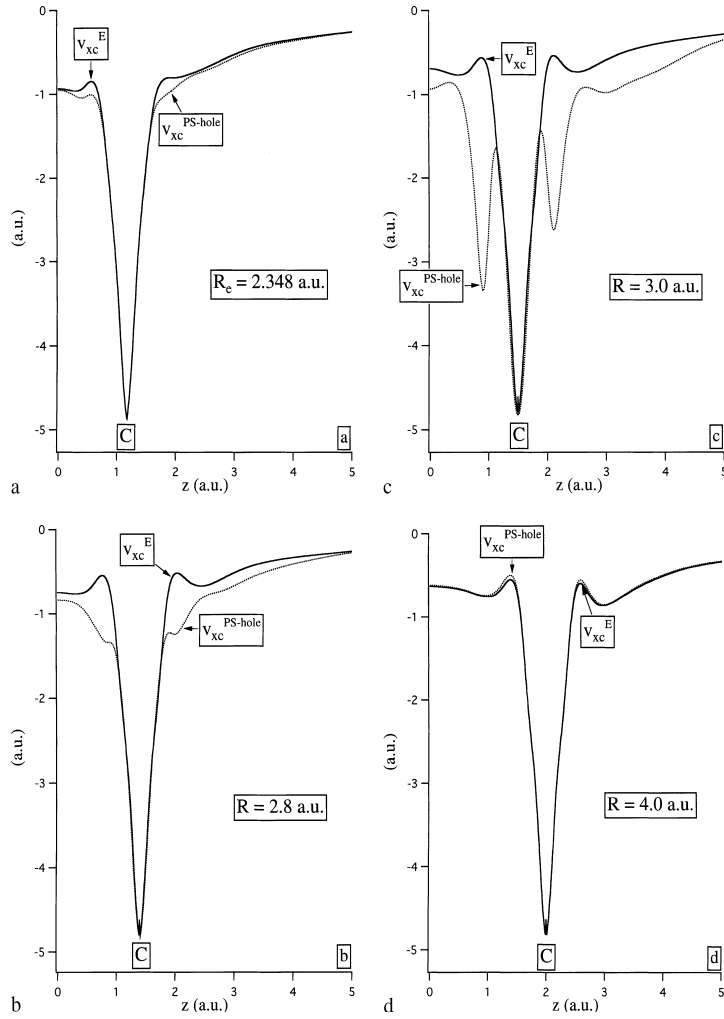
$$\tilde{\varphi}_i(\mathbf{r}) = \sum_j U_{ij} \varphi_j(\mathbf{r}) \quad (254)$$

Since these orbitals are linear combinations of degenerate orbitals, they are again eigenfunctions of the Kohn-Sham single-particle Hamiltonian for the highest occupied level. We can now write the density as

$$n(\mathbf{r}) = \sum_{\epsilon_i < \mu} |\varphi_i(\mathbf{r})|^2 + \sum_{\epsilon_k = \mu} n_k |\tilde{\varphi}_k(\mathbf{r})|^2 \quad (255)$$

with occupation numbers  $n_k$  between 0 and 1. We see that for the case of a degenerate ground state we have to solve Eq.(250) together with Eq.(255) in which also the coefficients  $n_k$  must be determined. When do we need fractional occupation numbers in practice? In practice one sometimes finds that when solving the Kohn-Sham equations with occupations equal to one that the converged solution has a hole below the highest level. This happens for instance for the iron atom within the local density approximation [24]. This is an indication that the true Kohn-Sham density could be an E-V-density. In practice the lowest energy state is then obtained by a procedure called "evaporation of the hole". In this method one increases the occupation of the hole while decreasing the occupation of the highest level until both levels are degenerate [24, 25]. The matter has been investigated in detail by Schipper et al. [26, 27]. These authors calculated by CI-methods accurate charge densities for a couple of molecules. Subsequently they constructed the Kohn-Sham potentials that generate these

densities. A particularly interesting case is the  $C_2$  molecule [26]. When one tries to construct a Kohn-Sham potential that produces the ground state density of the  $C_2$  molecule using occupation numbers equal to one, i.e. for a pure state, one finds that the solution corresponds to a state with a hole below the highest occupied level. This is then not a proper Kohn-Sham state since it is not the state of lowest energy for the corresponding potential, but an excited state. If one then tries to construct an ensemble solution by the technique of "evaporation of the hole", one does find a proper ground state ensemble for the Kohn-Sham system. From this we can conclude that the ground state density of the  $C_2$  molecule is a noninteracting E-V-density but not a noninteracting PS-V-density. This means that the extension of density functionals to E-V-densities is not only of theoretical, but also practical interest. As an illustration we display in Figure 4, the exchange-correlation potentials of the  $C_2$  molecule for four bonding distances. The potentials are plotted along the  $C-C$  bond axis as functions of the distance  $z$  from the bond midpoint. The corresponding bond distances  $R(C-C)$  are displayed in the inset. The potentials  $v_{xc}^{PS-hole}$  correspond to the exchange-correlation potentials of the improper Kohn-Sham solutions with a hole. The corresponding state is a pure state consisting of a single Slater determinant. The potentials  $v_{xc}^E$  are the Kohn-Sham potentials corresponding to a ground state ensemble. Both  $v_{xc}^{PS-hole}$  and  $v_{xc}^E$  give an accurate representation of the true density of the molecule, although the accuracy attained with  $v_{xc}^E$  is a bit higher. The potential  $v_{xc}^E$  has the features found in many diatomic molecules, i.e. the usual well around the atom, the small intershell peaks and a plateau around the bond midpoint. The potential  $v_{xc}^{PS-hole}$  on the other hand, is heavily distorted as compared to  $v_{xc}^E$ . This may be explained by the fact that the wavefunction of the  $C_2$  molecule has a strong multideterminantal character. With this we mean that the simple Hartree-Fock approximation has a relatively small coefficient in the CI-expansion of the wave function. The distortions in  $v_{xc}^{PS-hole}$  therefore appear to be a price we have to pay for producing the density of such a strongly multideterminantal state with a single Slater determinant. The use of an ensemble formulation of Kohn-Sham theory seems therefore especially relevant in cases of strong electron correlations. Other examples are provided by near-degeneracy situations such as in avoided crossings [25] and the  $H_2 + H_2$  reaction [27]. A recent discussion on Kohn-Sham theory for ensembles can be found in Ref. [28] which also gives the beryllium series as an explicit example of systems which are ensemble  $v$ -representable but not pure state  $v$ -representable.



**Figure 4:** Exchange-correlation potentials producing the accurate interacting ground state density of the  $C_2$  molecule at various bonding distances. The potential  $v_{xc}^E$  is the exchange-correlation potential for a ground state ensemble. The potential  $v_{xc}^{PS-hole}$  is an exchange-correlation potential that reproduces the same density for a single Slater determinant with a hole.

## 16. The gradient expansion

Until now we only considered the formal framework of density functional theory. However, the theory would be of little use if we would not be able to construct good approximate functionals for the exchange-correlation energy and exchange-correlation functional. Historically the first approximation for the exchange-correlation functional to be used was the local density approximation. In this approximation the exchange-correlation functional is taken to be

$$E_{xc}^{LDA}[n] = \int d^3r \epsilon_{xc}(n(\mathbf{r})) \quad (256)$$

where  $\epsilon_{xc}(n)$  is the exchange-correlation energy per volume unit for a homogeneous electron gas with density  $n$ . We therefore treat the inhomogeneous system locally as an electron gas. This simple and crude approximation turns out to be surprisingly succesful for realistic and very inhomogeneous systems although one would expect that the LDA would only be accurate for systems with slowly varying densities. The LDA therefore seems a suitable starting point for more accurate approximations. In this section we will show that the LDA is in fact the first term in a systematic expansion of the exchange-correlation functional in terms of spatial derivatives with respect to the density. This expansion is commonly referred to as the gradient expansion [5, 29, 30] and has the following form

$$\begin{aligned} E_{xc}[n] &= E_{xc}^{LDA}[n] + \int d^3r g_1(n(\mathbf{r}))(\nabla n(\mathbf{r}))^2 \\ &+ \int d^3r g_2(n(\mathbf{r}))(\nabla^2 n(\mathbf{r}))^2 + \dots \end{aligned} \quad (257)$$

where the functions  $g_i(n)$  are uniquely determined by the density response functions (of arbitrary order) of the homogeneous electron gas. The gradient expansion presents an, in principle, exact way to construct the exchange-correlation functional for solids, provided the series converges. We will come back to the question of convergence. To derive the gradient expansion we start out by expanding the exact exchange-correlation energy functional around its homogeneous electron gas value  $n_0$  as follows

$$\begin{aligned} E_{xc}[n] &= E_{xc}[n_0] + \\ &\sum_{m=1}^{\infty} \frac{1}{m!} \int d^3r K_{xc}^{(m)}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) \delta n(\mathbf{r}_1) \dots \delta n(\mathbf{r}_m) \end{aligned} \quad (258)$$

where  $d^3r = d^3r_1 \dots d^3r_m$  and  $n(\mathbf{r}) = n_0 + \delta n(\mathbf{r})$ . We further defined

$$K_{xc}^{(m)}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) = \frac{\delta^m E_{xc}}{\delta n(\mathbf{r}_1) \dots \delta n(\mathbf{r}_m)} \Big|_{n=n_0} \quad (259)$$

The first term  $E_{xc}[n_0]$  in Eq.(258) is the exchange-correlation energy of a homogeneous system with constant density  $n_0$  and is therefore a function of  $n_0$  rather than a functional. We will therefore write this term as  $E_{xc}(n_0)$ . This function is by now well-known from extensive investigations of the homogeneous electron gas [31]. Since the electron gas has translational, rotational and inversion symmetry the functions  $K_{xc}^{(m)}$  satisfy

$$K_{xc}^{(m)}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) = K_{xc}^{(m)}(n_0; \mathbf{r}_1 + \mathbf{a} \dots \mathbf{r}_m + \mathbf{a}) \quad (260)$$

$$K_{xc}^{(m)}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) = K_{xc}^{(m)}(n_0; R\mathbf{r}_1 \dots R\mathbf{r}_m) \quad (261)$$

$$K_{xc}^{(m)}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) = K_{xc}^{(m)}(n_0; -\mathbf{r}_1 \dots -\mathbf{r}_m) \quad (262)$$

where  $\mathbf{a}$  is an arbitrary translation vector and where  $R$  is an arbitrary rotation matrix. Furthermore, the function  $K_{xc}^{(m)}$  has full permutational symmetry, i.e.

$$K_{xc}^{(m)}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) = K_{xc}^{(m)}(n_0; \mathbf{r}_{P(1)} \dots \mathbf{r}_{P(m)}) \quad (263)$$

for an arbitrary permutation  $P$  of the indices  $1 \dots m$ . If we choose  $\mathbf{a} = -\mathbf{r}_1$  in Eq. (260) we see that

$$\begin{aligned} K_{xc}^{(m)}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) &= K_{xc}^{(m)}(n_0; \mathbf{0}, \mathbf{r}_2 - \mathbf{r}_1 \dots \mathbf{r}_m - \mathbf{r}_1) \\ &= L^{(m)}(n_0; \mathbf{r}_2 - \mathbf{r}_1 \dots \mathbf{r}_m - \mathbf{r}_1) \end{aligned} \quad (264)$$

where the latter equation defines the function  $L^{(m)}$  as a function of  $m - 1$  variables. Let us give some specific examples. The function  $K_{xc}^{(1)}$  is given by

$$K_{xc}^{(1)}(n_0; \mathbf{r}_1) = \frac{\delta E_{xc}}{\delta n(\mathbf{r}_1)}|_{n=n_0} = v_{xc}(n_0) \quad (265)$$

and we see that this function is simply the exchange-correlation potential of the electron gas which, due to translational invariance, does not depend on  $\mathbf{r}_1$ . Since  $\delta n(\mathbf{r})$  integrates to zero the term with  $K_{xc}^{(1)}$  in the expansion Eq.(258) does not contribute to  $E_{xc}[n]$ . The first nontrivial term is therefore

$$K_{xc}^{(2)}(n_0; \mathbf{r}_1, \mathbf{r}_2) = \frac{\delta^2 E_{xc}}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)}|_{n=n_0} = L^{(2)}(n_0; \mathbf{r}_2 - \mathbf{r}_1) \quad (266)$$

which leads to an expansion of the form

$$E_{xc}[n] = E_{xc}(n_0) + \frac{1}{2} \int d^3r_1 d^3r_2 L^{(2)}(n_0; \mathbf{r}_2 - \mathbf{r}_1) \delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2) + \dots \quad (267)$$

The function  $L^{(2)}$  (often denoted by  $K_{xc}$  in the literature) has been the subject of many investigations [32, 33]. Let us now go back to the more general case. If we introduce the Fourier transform of a function  $f$  as follows

$$\tilde{f}(\mathbf{q}_1 \dots \mathbf{q}_m) = \int d^3r f(\mathbf{r}_1 \dots \mathbf{r}_m) e^{-i\mathbf{q}_1 \cdot \mathbf{r}_1 - \dots - i\mathbf{q}_m \cdot \mathbf{r}_m} \quad (268)$$

then

$$\tilde{K}_{xc}^{(m)}(n_0; \mathbf{q}_1 \dots \mathbf{q}_m) = (2\pi)^3 \delta(\mathbf{q}_1 + \dots + \mathbf{q}_m) \tilde{L}^{(m)}(n_0; \mathbf{q}_2 \dots \mathbf{q}_m) \quad (269)$$

The expansion for  $E_{xc}$  then becomes

$$E_{xc}[n] = E_{xc}(n_0) + \sum_{m=1}^{\infty} \frac{1}{m!} \int \frac{d^{3m}q}{(2\pi)^{3m}} \tilde{K}_{xc}^{(m)}(n_0; \mathbf{q}_1 \dots \mathbf{q}_m) \delta \tilde{n}(\mathbf{q}_1) \dots \delta \tilde{n}(\mathbf{q}_m) \quad (270)$$

where  $d^{3m}q = d^3q_1 \dots d^3q_m$ . This can also be written in terms of the functions  $L^{(m)}$  as follows

$$E_{xc}[n] = E_{xc}(n_0) + \sum_{m=1}^{\infty} \frac{1}{m!} \int \frac{d^3q_2}{(2\pi)^3} \dots \frac{d^3q_m}{(2\pi)^3} \tilde{L}^{(m)}(n_0; \mathbf{q}_2 \dots \mathbf{q}_m) \times \delta \tilde{n}(-\mathbf{q}_2 - \dots - \mathbf{q}_m) \delta \tilde{n}(\mathbf{q}_2) \dots \delta \tilde{n}(\mathbf{q}_m) \quad (271)$$

The gradient expansion is then obtained by expanding  $L^{(m)}$  in powers of  $\mathbf{q}_i$  around  $\mathbf{q}_i = 0$  and subsequently transforming back to real space. If we do this our final expansion will then still depend on our reference density  $n_0$  which is undesirable for application of the functional to general systems. However, we will show that we can get rid of this dependence on  $n_0$  by doing infinite resummations. The key formula that will enable us to do these resummations is the following first order change of  $K_{xc}^{(m)}$ :

$$\delta K_{xc}^{(m)}(\mathbf{r}_1 \dots \mathbf{r}_m) = \int d^3r K_{xc}^{(m+1)}(n_0; \mathbf{r}, \mathbf{r}_1 \dots \mathbf{r}_m) \delta n(\mathbf{r}) \quad (272)$$

If we take  $\delta n(\mathbf{r}) = \delta n_0$  to be a constant change we obtain

$$\frac{\partial K_{xc}^{(m)}}{\partial n_0}(n_0; \mathbf{r}_1 \dots \mathbf{r}_m) = \int d^3r K_{xc}^{(m+1)}(n_0; \mathbf{r}, \mathbf{r}_1 \dots \mathbf{r}_m) \quad (273)$$

Note that by taking  $\delta n(\mathbf{r}) = \delta n_0$  we violate the condition that  $\delta n(\mathbf{r})$  integrates to zero. Nevertheless Eq.(273) can alternatively be derived directly from the properties of the response functions [30] and is related to a generalized form of the well-known compressibility sumrule of the electron gas. An important special case is obtained for  $m = 1$ :

$$\begin{aligned} \frac{\partial v_{xc}}{\partial n_0} &= \frac{\partial K_{xc}^{(1)}}{\partial n_0}(n_0) = \int d^3r_2 K_{xc}^{(2)}(n_0; \mathbf{r}_1, \mathbf{r}_2) \\ &= \int d^3r_2 L^{(2)}(n_0; \mathbf{r}_2 - \mathbf{r}_1) = \tilde{L}^{(2)}(\mathbf{q} = \mathbf{0}) \end{aligned} \quad (274)$$



We see that the  $\mathbf{q} = 0$  value of  $\tilde{L}^{(2)}$  can be directly calculated from the knowledge of  $v_{xc}(n_0)$ . For  $m \geq 2$  relation (273) directly implies the following relation between  $L^{(m)}$  and  $L^{(m+1)}$

$$\frac{\partial L^{(m)}}{\partial n_0}(n_0; \mathbf{q}_2 \dots \mathbf{q}_m) = L^{(m+1)}(n_0; -\mathbf{q}_2 - \dots - \mathbf{q}_m, \mathbf{q}_2 \dots \mathbf{q}_m) \quad (275)$$

The importance of this formula will become clear if we work out, as an explicit example, the lowest order in the gradient expansion. From the symmetry properties of  $K_{xc}^{(m)}$  one finds that its Fourier transform has the following expansion in powers of  $\mathbf{q}_i$ :

$$\begin{aligned} \tilde{K}_{xc}^{(m)}(n_0; \mathbf{q}_1 \dots \mathbf{q}_m) &= (2\pi)^3 \delta(\mathbf{q}_1 + \dots + \mathbf{q}_m) \\ &\times (K_0^{(m)} + K_1^{(m)} P_1^{(m)}(\mathbf{q}_1 \dots \mathbf{q}_m) + K_2^{(m)} P_2^{(m)}(\mathbf{q}_1 \dots \mathbf{q}_m) + \dots) \end{aligned} \quad (276)$$

in which the  $K_i^{(m)}$  are coefficients and  $P_i^{(m)}$  are symmetric polynomials. This is a direct consequence of the permutational symmetry of  $K_{xc}$ . The first polynomial  $P_1^{(m)}$  (taking into account the  $\delta$ -function) has the explicit form

$$P_1^{(m)}(\mathbf{q}_1 \dots \mathbf{q}_m) = \mathbf{q}_1^2 + \dots + \mathbf{q}_m^2 \quad (277)$$

and is invariant under permutation of the indices, i.e. it transforms according to a one-dimensional representation of the permutation group. More details on the group theoretical treatment of these response functions can be found in the work of Svendsen and von Barth [34]. From the properties of  $\tilde{K}_{xc}^{(m)}$  we find that for  $m \geq 2$  the function  $L^{(m)}$  has the following expansion

$$L^{(m)}(n_0; \mathbf{q}_2 \dots \mathbf{q}_m) = L_0^{(m)}(n_0) + L_1^{(m)}(n_0) p^{(m)}(\mathbf{q}_2 \dots \mathbf{q}_m) + \dots \quad (278)$$

where the polynomial  $p^{(m)}$  is given by

$$\begin{aligned} p^{(m)}(\mathbf{q}_2 \dots \mathbf{q}_m) &= (-\mathbf{q}_2 - \dots - \mathbf{q}_m)^2 + \mathbf{q}_2^2 + \dots + \mathbf{q}_m^2 \\ &= 2 \sum_{i=2}^m \mathbf{q}_i^2 - 2 \sum_{i>j \geq 2}^m \mathbf{q}_i \cdot \mathbf{q}_j \end{aligned} \quad (279)$$

It is easily seen that this polynomial has the property

$$p^{(m+1)}(-\mathbf{q}_2 - \dots - \mathbf{q}_m, \mathbf{q}_2 \dots \mathbf{q}_m) = p^{(m)}(\mathbf{q}_2 \dots \mathbf{q}_m) \quad (280)$$

If we use this property together with Eq.(278) and Eq.(275) we obtain for the coefficients in the expansion of  $L^{(m)}$  the following equations

$$\frac{\partial L_0^{(m)}}{\partial n_0} = L_0^{(m+1)}(n_0) \quad (281)$$

$$\frac{\partial L_1^{(m)}}{\partial n_0} = L_1^{(m+1)}(n_0) \quad (282)$$

where  $m \geq 2$ . Together with

$$\tilde{L}^{(2)}(\mathbf{q} = \mathbf{0}) = \frac{\partial v_{xc}}{\partial n_0}(n_0) = \frac{\partial^2 \epsilon_{xc}}{\partial n_0^2}(n_0) \quad (283)$$

where  $\epsilon_{xc}(n_0)$  is the exchange energy per volume unit of the electron gas, this yields

$$L_0^{(m)}(n_0) = \frac{\partial^m \epsilon_{xc}}{\partial n_0^m}(n_0) \quad (284)$$

$$L_1^{(m)}(n_0) = \frac{\partial^{m-2} L_1^{(2)}}{\partial n_0^{m-2}}(n_0) \quad (285)$$

It is these two equations that will allow us to eliminate the dependence on  $n_0$  in the lowest order gradient expansion. If we insert the explicit form of  $L^{(m)}$  of Eq.(278) into Eq.(271) and Fourier transform back to real space we obtain

$$\begin{aligned} E_{xc}[n] = & E_{xc}(n_0) + \\ & \sum_{m=1}^{\infty} \frac{1}{m!} L_0^{(m)}(n_0) \int d^3r (\delta n(\mathbf{r}))^m + \\ & \sum_{m=2}^{\infty} \frac{1}{m!} L_1^{(m)}(n_0) m(m-1) \int d^3r (\nabla \delta n(\mathbf{r}))^2 (\delta n(\mathbf{r}))^{m-2} + \dots \end{aligned} \quad (286)$$

Since  $\nabla \delta n(\mathbf{r}) = \nabla n(\mathbf{r})$  this can be rewritten with help of Eq.(284) and Eq.(285) as

$$\begin{aligned} E_{xc}[n] = & E_{xc}(n_0) + \\ & \sum_{m=1}^{\infty} \frac{1}{m!} \frac{\partial^m \epsilon_{xc}(n_0)}{\partial n_0^m} \int d^3r (\delta n(\mathbf{r}))^m + \\ & \sum_{m=2}^{\infty} \frac{1}{(m-2)!} \frac{\partial^{m-2} L_1^{(2)}(n_0)}{\partial n_0^{m-2}} \int d^3r (\nabla n(\mathbf{r}))^2 (\delta n(\mathbf{r}))^{m-2} + \dots \end{aligned} \quad (287)$$

We see that the first two terms simply give the expansion of the LDA functional around the constant density  $n_0$ , i.e.

$$E_{xc}^{LDA}[n] = \int d^3r \epsilon_{xc}(n_0 + \delta n(\mathbf{r})) \quad (288)$$

whereas the third term involves an expansion of the coefficient  $L_1^{(2)}(n_0 + \delta n(\mathbf{r}))$  around  $n_0$ . We obtain

$$E_{xc}[n] = E_{xc}^{LDA}[n] + \int d^3r L_1^{(2)}(n(\mathbf{r})) (\nabla n(\mathbf{r}))^2 + \dots \quad (289)$$

and we see that we succeeded in eliminating the dependence on  $n_0$  in the gradient expansion. Moreover we see that the local density approximation naturally appears as the first term in the gradient expansion. Furthermore we find that the coefficient  $g_1(n)$  in our first equation (257) is completely determined by the  $\mathbf{q}$ -expansion of the function  $\tilde{L}^{(2)}(n_0; \mathbf{q})$  to order  $\mathbf{q}^2$ . We also see that the replacement  $n_0 \rightarrow n(\mathbf{r})$  requires a resummation over response functions of arbitrary order. The dependence on  $n_0$  can also be removed to higher order in powers of  $\mathbf{q}$ . For an explicit example up to order  $\mathbf{q}^4$  we refer again to Svendsen and von Barth [34].

Let us now address the question of convergence of the gradient expansion. This question has been investigated for the gradient expansion of the exchange-energy functional for which a comparison with exact exchange energies is possible. For this case the analytic form of  $\tilde{L}^{(2)}(n_0; \mathbf{q})$  is known from the impressive work of Engel and Vosko [35, 36] and some higher order gradient coefficients have been determined by Svendsen, Springer and von Barth [34, 37]. One finds [37] that the gradient expansion performs very well for metallic systems, but that the quality deteriorates as soon as the system acquires an energy gap. This may not be so surprising if one realizes that the appearance of a gap drastically changes the low  $\mathbf{q}$ -behavior of the response functions  $K_{xc}^{(m)}$  which determine the gradient coefficients [38]. This means that the standard gradient expansion can not deal with insulators or finite systems (which may be modelled as insulators by repeating them periodically with a large lattice constant). Further progress along the lines of the gradient expansion may be obtained by study of the so-called gapped electron gas [39]. Currently the most fruitful approach to the construction of simple and accurate functionals is the so-called Generalized Gradient Approximation (GGA) [40, 41]. In this approach one specifies a form of the pair-correlation function of the many-electron system and determines the parameters in this function by sumrules and information from the straightforward gradient expansion. These functionals have lead to large improvements in molecular binding energies as compared to the local density approximation [42]. However, since the approach is not systematic it is difficult to improve the quality of the current GGA functionals.

## 17. The optimized potential method and the $e^2$ -expansion

In this section we will describe a second systematic method to construct density functionals, namely perturbation theory starting from the Kohn-Sham Hamiltonian [43, 44]. The method is based on traditional perturbation theory and is comparable in computational cost. For this reason the method is less suited to the calculation of properties of large systems. However, the method has the theoretical advantage that it can be used as a

benchmark to test the quality of different approximate density functionals. We consider the Hamiltonian

$$\hat{H}_\epsilon = \hat{H}_s + \epsilon(\hat{H} - \hat{H}_s) = \hat{H}_s + \epsilon(\hat{W} - \hat{V}_{Hxc}) \quad (290)$$

where

$$\hat{W} = \sum_{i>j}^N \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (291)$$

$$\hat{V}_{Hxc} = \sum_{i=1}^N v_H(\mathbf{r}_i) + v_{xc}(\mathbf{r}_i) \quad (292)$$

where  $e^2$  is the square of the electronic charge and  $v_H$  is the usual Hartree potential

$$v_H(\mathbf{r}) = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (293)$$

and  $v_{xc}$  the exchange-correlation potential. The perturbation term is simply the difference between the true and the Kohn-Sham Hamiltonian and we are interested in the case  $\epsilon = 1$  although this makes expansion in powers of  $\epsilon$  rather doubtful. We will come back to the point of convergence later. We can now do standard perturbation theory and obtain the ground state energy

$$E(\epsilon) = E_s + \epsilon E^{(1)} + \epsilon^2 E^{(2)} + \dots \quad (294)$$

where  $E_s$  is ground state energy of the auxiliary Kohn-Sham system, i.e. simply a sum over orbital energies and the terms  $E^{(i)}$  is the energy to order  $i$  in powers of  $\epsilon$ . The first two terms are explicitly given by [43, 44]

$$E^{(1)} = \langle \Phi_s | \hat{W} - \hat{V}_{Hxc} | \Phi_s \rangle \quad (295)$$

$$E^{(2)} = \sum_{i=1}^{\infty} \frac{|\langle \Phi_s | \hat{W} - \hat{V}_{Hxc} | \Phi_{s,i} \rangle|^2}{E_s - E_{s,i}} \quad (296)$$

where  $E_{s,i}$  and  $\Phi_{s,i}$  are the excited state energies and wave functions of the Kohn-Sham system. We now note that the energies  $E^{(i)}$  are implicit functionals of the density through their dependence on the Kohn-Sham potential, orbitals, and energies, i.e.

$$E^{(i)}[n] = E^{(i)}[\{\varphi_k[n]\}, \{\epsilon_k[n]\}, v_{xc}[n]] \quad (297)$$

This follows directly from the Hohenberg-Kohn theorem applied to a non-interacting system. The density  $n$  uniquely determines the Kohn-Sham potential  $v_s$  (up to a constant) and therefore the also the orbitals (up to a phase factor) and eigenvalues (up to constant). The arbitrariness with

respect to a constant shift and with respect to the phase factor cancels out in the energy expression and therefore the  $i$ -th order energy becomes a pure density functional. We therefore have the following series of implications

$$n(\mathbf{r}) \rightarrow v_s(\mathbf{r}) \rightarrow \{\varphi_k(\mathbf{r}), \epsilon_k\} \rightarrow E^{(i)} \quad (298)$$

Note that the perturbation theory that we constructed is not yet in a form that we can use in practical calculations. This is because the perturbing Hamiltonian contains the exchange-correlation potential which is unknown from the start and has to be determined self-consistently from the perturbation series. However, the equations can be simplified if we expand the energies and potentials in powers of the interaction strength  $e^2$  and take  $\epsilon = 1$ . This leads to the following set of equations [44]

$$\begin{aligned} E[n] &= T_s[n] + \int d^3r n(\mathbf{r}) v(\mathbf{r}) \\ &+ \frac{e^2}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \sum_{i=1}^{\infty} e^{2i} E_{xc}^{(i)} \end{aligned} \quad (299)$$

$$v_{Hxc}(\mathbf{r}) = v_H(\mathbf{r}) + \sum_{i=1}^{\infty} e^{2i} v_{xc}^{(i)}(\mathbf{r}) \quad (300)$$

$$v_{xc}^{(i)}(\mathbf{r}) = \frac{\delta E_{xc}^{(i)}}{\delta n(\mathbf{r})} \quad (301)$$

The  $e^2$  and  $e^4$  terms in the expansion of the exchange-correlation energy have the explicit form

$$e^2 E_{xc}^{(1)}[n] = \langle \Phi_s | \hat{W} | \Phi_s \rangle - \frac{e^2}{2} \int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (302)$$

and

$$e^4 E_{xc}^{(2)}[n] = \sum_{i=1}^{\infty} \frac{|\langle \Phi_s | \hat{W} - \hat{V}_H - e^2 \hat{V}_{xc}^{(1)} | \Phi_{s,i} \rangle|^2}{E_s - E_{s,i}} \quad (303)$$

The term of order  $e^2$  can be written explicitly in terms of the Kohn-Sham orbitals as follows:

$$E_{xc}^{(1)}[n] = -\frac{1}{2} \sum_{k,l=1}^N \int d^3r d^3r' \frac{\varphi_k^*(\mathbf{r}) \varphi_l(\mathbf{r}) \varphi_l^*(\mathbf{r}') \varphi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (304)$$

We see that this expression has exactly the same form as the usual expression of the exchange energy within the Hartree-Fock approximation. The difference, however, is that the orbitals in this expression are Kohn-Sham

orbitals which, in contrast to the Hartree-Fock orbitals, are eigenfunctions of a single-particle Hamiltonian with a local potential. The numerical value of  $E_{xc}^{(1)}[n]$  and the Hartree-Fock exchange will therefore in general differ from each other. However, because of the similarity to the Hartree-Fock definition of exchange we will define the exchange functional within density functional theory to be  $E_x[n] = E_{xc}^{(1)}[n]$ . Corresponding to the exchange-functional there is a local exchange potential defined as

$$v_x(\mathbf{r}) = \frac{\delta E_x}{\delta n(\mathbf{r})} = \frac{\delta E_{xc}^{(1)}}{\delta n(\mathbf{r})} = v_{xc}^{(1)}(\mathbf{r}) \quad (305)$$

We see from Eq.(303) that we need to know this potential in order to calculate the  $e^4$  contribution to the exchange-correlation energy. This is a general feature of the present perturbation theory. In order to calculate  $E_{xc}^{(i)}$  we need to calculate  $v_{xc}^{(i-1)}$  first. Let us therefore start by calculating  $v_x$ . For this we have to calculate the first order change  $\delta E_x$  in the exchange functional due to a change  $\delta n$  in the density. Since densities and potentials are in 1-1-correspondence this task amounts to calculating the change in  $E_x$  due to a change  $\delta v_s$  in the Kohn-Sham potential. This is readily done by perturbation theory. The change  $\delta \varphi_k$  and  $\delta \epsilon_k$  of the orbitals and orbital energies of the Kohn-Sham system due to a small change  $\delta v_s$  in the potential is given by solution of the equation

$$\left( -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) - \epsilon_k \right) \delta \varphi_k(\mathbf{r}) = (\delta \epsilon_k - \delta v_s(\mathbf{r})) \varphi_k(\mathbf{r}) \quad (306)$$

This gives

$$\delta \epsilon_k = \int d^3r \varphi_k^*(\mathbf{r}) \varphi_k(\mathbf{r}) \delta v_s(\mathbf{r}) \quad (307)$$

$$\delta \varphi_k(\mathbf{r}) = - \int d^3r' G_k(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}') \delta v_s(\mathbf{r}') \quad (308)$$

$$G_k(\mathbf{r}, \mathbf{r}') = \sum_{l \neq k} \frac{\varphi_l(\mathbf{r}) \varphi_l^*(\mathbf{r}')}{\epsilon_l - \epsilon_k} \quad (309)$$

From these equations we obtain the following functional derivatives

$$\frac{\delta \epsilon_k}{\delta v_s(\mathbf{r})} = \varphi_k^*(\mathbf{r}) \varphi_k(\mathbf{r}) \quad (310)$$

$$\frac{\delta \varphi_k(\mathbf{r})}{\delta v_s(\mathbf{r}')} = -G_k(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}') \quad (311)$$

The density change  $\delta n$  is given by

$$\delta n(\mathbf{r}) = \sum_{k=1}^N \varphi_k^*(\mathbf{r}) \delta \varphi_k(\mathbf{r}) + c.c. = \int d^3r' \chi_s(\mathbf{r}, \mathbf{r}') \delta v_s(\mathbf{r}') \quad (312)$$

where we defined the static density response function  $\chi_s$  of the Kohn-Sham system by

$$\chi_s(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} = - \sum_{k=1}^N \varphi_k^*(\mathbf{r}) G_k(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}') + c.c. \quad (313)$$

We can now readily derive the following integral equation for  $v_x$ :

$$\Lambda_x(\mathbf{r}) = \frac{\delta E_x}{\delta v_s(\mathbf{r})} = \int d^3 r' \frac{\delta E_x}{\delta n(\mathbf{r}')} \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} = \int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') \quad (314)$$

where the inhomogeneity  $\Lambda_x$  is given by

$$\Lambda_x(\mathbf{r}) = - \sum_{k=1}^N \int d^3 r' \frac{\delta E_x}{\delta \varphi_k(\mathbf{r}')} G_k(\mathbf{r}', \mathbf{r}) \varphi_k(\mathbf{r}) + c.c. \quad (315)$$

Since both  $\Lambda_x$  and  $\chi_s$  are given as explicit functionals of the Kohn-Sham orbitals and orbital energies, the exchange potential can be found from simultaneous solution of the equations

$$\epsilon_k \varphi_k(\mathbf{r}) = \left( -\frac{1}{2} \nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) + e^2 v_x(\mathbf{r}) \right) \varphi_k(\mathbf{r}) \quad (316)$$

$$\Lambda_x(\mathbf{r}) = \int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}') v_x(\mathbf{r}') \quad (317)$$

Once we have solved these equations and determined  $v_x$  we can go on and calculate  $E_{xc}^{(2)}$  from Eq.(303). To calculate the  $e^6$  contribution to the exchange-correlation energy we first have to evaluate  $v_{xc}^{(2)}$ . This potential is the solution of the integral equation

$$\Lambda_{xc}^{(2)}(\mathbf{r}) = \frac{\delta E_{xc}^{(2)}}{\delta v_s(\mathbf{r})} = \int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}') v_{xc}^{(2)}(\mathbf{r}') \quad (318)$$

Since  $E_{xc}^{(2)}$  is an explicit functional of the orbitals, orbital energies and  $v_x$  the inhomogeneity  $\Lambda_{xc}^{(2)}$  can be calculated from

$$\begin{aligned} \Lambda_{xc}^{(2)}(\mathbf{r}) &= \left[ \sum_{k=1}^{\infty} \int d^3 r' \frac{\delta E_{xc}^{(2)}}{\delta \varphi_k(\mathbf{r}')} \frac{\delta \varphi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right] \\ &+ \sum_{k=1}^{\infty} \int d^3 r' \frac{\delta E_{xc}^{(2)}}{\delta \epsilon_k} \frac{\delta \epsilon_k}{\delta v_s(\mathbf{r})} + \int d^3 r' \frac{\delta E_{xc}^{(2)}}{\delta v_x(\mathbf{r}')} \frac{\delta v_x(\mathbf{r}')}{\delta v_s(\mathbf{r})} \end{aligned} \quad (319)$$

All terms in this equation are explicitly known, except for the term  $\delta v_x / \delta v_s$ . However, for this term we can find an integral equation by differentiation

of Eq.(317) with respect to  $v_s$ :

$$\frac{\delta \Lambda_x(\mathbf{r}_1)}{\delta v_s(\mathbf{r}_2)} = \int d^3 r_3 \frac{\delta \chi_s(\mathbf{r}_1, \mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)} v_x(\mathbf{r}_3) + \int d^3 r_3 \chi_s(\mathbf{r}_1, \mathbf{r}_3) \frac{\delta v_x(\mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)} \quad (320)$$

Since both  $\Lambda_x$  and  $\chi_s$  are explicitly known in terms of orbitals and orbital energies their derivatives with respect to  $v_s$  are also explicitly known in terms of these quantities (see reference [44] for more details) and therefore Eq.(320) determines  $\delta v_x / \delta v_s$  uniquely. So we see that in order to determine  $v_{xc}^{(2)}$  we have to solve two integral equations. For realistic systems these equations have only be solved approximately (for an explicit solution of Eq.(320) see reference [34])). From  $v_{xc}^{(2)}$  one could go on along the same lines to determine  $E_{xc}^{(3)}$  and subsequently  $v_{xc}^{(3)}$ . The determination of these higher order energies and potentials becomes more involved. Nevertheless, the perturbation series represents an explicit construction procedure for the exact exchange-correlation energy and potential, provided that the series converges. Before we go on to discuss the convergence properties of this series, let us briefly review the first order equations from a different viewpoint. It is readily seen that one can write the total energy to order  $e^2$ , which we denote by  $E_1[n]$ , as

$$\begin{aligned} E_1[n] &= T_s[n] + \int d^3 r n(\mathbf{r}) v(\mathbf{r}) + \frac{e^2}{2} \int d^3 r d^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + e^2 E_x[n] \\ &= \langle \Phi_s | \hat{H} | \Phi_s \rangle \end{aligned} \quad (321)$$

This is just the expectation value of the true Hamiltonian  $\hat{H}$  of the system with the Kohn-Sham wave function  $|\Phi_s\rangle$ . Because of the 1-1-correspondence between the density  $n$  and the potential  $v_s$  we can also regard  $E_1$  as a functional of the potential  $v_s$ , i.e.

$$E_1[v_s] = \langle \Phi_s[v_s] | \hat{H} | \Phi_s[v_s] \rangle \quad (322)$$

We may now try to find an approximation to the true total energy of the system by choosing a local potential  $v_s$  that minimizes the energy expression  $E_1[v_s]$ . This means that we have to solve the variational equation

$$0 = \frac{\delta E_1}{\delta v_s(\mathbf{r})} = \sum_{k=1}^N \int d^3 r' \frac{\delta E_1}{\delta \varphi_k(\mathbf{r}')} \frac{\delta \varphi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \quad (323)$$

If one works out this expression one obtains equations that are identical to Eqns.(316) and (317). These equations were first derived by Talman and Shadwick [45]. Since in our procedure we optimized the energy of a Slater determinant wavefunction under the constraint that the orbitals



in the Slater determinant come from a local potential, the method is also known as the Optimized Potential Method (OPM). We have therefore obtained the result that the OPM and the expansion to order  $e^2$  are equivalent procedures. The OPM has many similarities to the Hartree-Fock approach. Within the Hartree-Fock approximation one minimizes the energy of a Slater determinant wavefunction under the constraint that the orbitals are orthonormal. One then obtains one-particle equations for the orbitals that contain a nonlocal potential. Within the OPM, on the other hand, one adds the additional requirement that the orbitals must satisfy single-particle equations with a local potential. Due to this constraint the OPM total energy  $E_1$  will in general be higher than the Hartree-Fock energy  $E_{HF}$ , i.e.  $E_1 \geq E_{HF}$ . We refer to [46, 47] for an application of the OPM method for molecules.

We finally make some comments on the calculation of functional derivatives in this section. We stress this point since careless use of the chain rule for differentiation has led to wrong results in the literature [48]. As an example we consider the exchange functional  $E_x$ . When we regard this functional as an explicit functional of the orbitals then the functional derivative with respect to  $\varphi_k$  is given by

$$\left( \frac{\delta E_x}{\delta \varphi_k(\mathbf{r})} \right)_e = - \sum_{i=1}^N \int d^3 r' \frac{\varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_k^*(\mathbf{r}') \quad (324)$$

where we used the subindex  $e$  to indicate that we regard the functional as an explicit orbital functional. This functional derivative represents the change in  $E_x$  due to a change  $\delta \varphi_k$  in orbital  $\varphi_k$ , while keeping all other orbitals fixed. Moreover, we regard  $\varphi_k$  and  $\varphi_k^*$  as independent variables. If we regard  $E_x$  as a density functional we must require that all orbitals are eigenfunctions of a noninteracting Hamiltonian with a local potential  $v_s$ . It is clear that we can never find a change  $\delta v_s$  in a local potential that induces a change in only one orbital while keeping the other orbitals fixed. If a potential changes one orbital  $\varphi_k$  to  $\varphi_k + \delta \varphi_k$  then all other orbitals will change too. The change in  $E_x$  regarded as a functional of  $v_s$  is then given by the functional derivative

$$\begin{aligned} \frac{\delta E_x}{\delta v_s(\mathbf{r})} &= \sum_{k=1}^N \int d^3 r' \left( \frac{\delta E_x}{\delta \varphi_k(\mathbf{r}')} \right)_e \frac{\delta \varphi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} \\ &+ \sum_{k=1}^N \int d^3 r' \left( \frac{\delta E_x}{\delta \varphi_k^*(\mathbf{r}')} \right)_e \frac{\delta \varphi_k^*(\mathbf{r}')}{\delta v_s(\mathbf{r})} \end{aligned} \quad (325)$$

We see that in this case the explicit orbital derivatives only occur in the sum in which all the orbital changes must be taken into account. We may

also introduce an implicit derivative  $(\delta E_x/\delta\varphi_k)_i$ , which can be given the meaning of giving the change in  $E_x$  if we know that there is a potential change  $\delta v_s$  that changes  $\varphi_k$  to  $\varphi_k + \delta\varphi_k$ . This implicit orbital derivative, which we denote by subindex  $i$  is expressed in terms of the explicit orbital derivatives as follows

$$\begin{aligned} \left(\frac{\delta E_x}{\delta\varphi_k(\mathbf{r})}\right)_i &= \sum_{i=1}^N \int d^3r' \left(\frac{\delta E_x}{\delta\varphi_i(\mathbf{r}')}\right)_e \frac{\delta\varphi_i(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})} \\ &+ \sum_{i=1}^N \int d^3r' \left(\frac{\delta E_x}{\delta\varphi_i^*(\mathbf{r}')}\right)_e \frac{\delta\varphi_i^*(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})} \end{aligned} \quad (326)$$

The derivatives  $\delta\varphi_i/\delta\varphi_k$  appear now to take into account that, if orbital  $\varphi_k$  changes to  $\varphi_k + \delta\varphi_k$  by some potential change  $\delta v_s$ , then the other orbitals  $\varphi_i$  change to  $\varphi_i + \delta\varphi_i$ . By using the implicit orbital derivative we regard  $E_x$  as a functional of the potential, or equivalently of the density, and we can therefore use the chain rule

$$\left(\frac{\delta E_x}{\delta\varphi_k(\mathbf{r})}\right)_i = \int d^3r' \frac{\delta E_x}{\delta n(\mathbf{r}')} \left(\frac{\delta n(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})}\right)_i = \int d^3r' v_x(\mathbf{r}') \left(\frac{\delta n(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})}\right)_i \quad (327)$$

In this equation  $(\delta n/\delta\varphi_k)_i$  is also an implicit derivative given by:

$$\left(\frac{\delta n(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})}\right)_i = \sum_{i=1}^N \int d^3r' \left[ \varphi_i^*(\mathbf{r}') \frac{\delta\varphi_i(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})} + \varphi_i(\mathbf{r}') \frac{\delta\varphi_i^*(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})} \right] \quad (328)$$

which should be compared to the explicit derivative

$$\left(\frac{\delta n(\mathbf{r}')}{\delta\varphi_k(\mathbf{r})}\right)_e = \varphi_k^*(\mathbf{r}') \quad (329)$$

for  $k = 1 \dots N$ . We stress that Eq.(327) is only true when using the implicit derivatives. If in Eq.(327) we replace the implicit derivatives by the explicit ones of Eq.(324) and Eq.(329) we obtain a result that is wrong. As pointed out this is due to the fact that a change in just one orbital can not be induced by a change in a local potential which in density functional theory is in 1-1-correspondence with the density. Most of the confusion can be avoided by regarding all functionals as functionals of the potential  $v_s$  and by calculating the change in the functionals by means of perturbation theory. In this way one can avoid use of the implicit orbital derivatives as in Eq.(326).

Let us finally come back to the question of convergence of the perturbation series. The perturbation series presented in this section is very similar to Møller-Plesset perturbation theory starting from the Hartree-Fock approximation. For the Møller-Plesset perturbation theory it is known that it is

in general divergent [49, 50, 51]. However, it is well-known that when carried out to low orders this perturbation theory gives reasonable answers. The Møller-Plesset perturbation series has therefore all the features of an asymptotic series [52]. Since the perturbation series in this section is very similar to the Møller-Plesset series it will in general also diverge. This has indeed been found in a perturbation theory on the basis of some approximate Kohn-Sham Hamiltonians [53]. Nevertheless, it has been found for the method presented in this section that low orders in perturbation theory give good results [54] and we conclude that our series give at least an asymptotic expansion for the exchange-correlation energy and potential.

## 18. Outlook and conclusions

In this work we have given an overview of the mathematical foundations of stationary density functional theory. We discussed in great detail the question of differentiability of the functionals and showed that the Kohn-Sham theory can be put on a solid basis for all practical purposes, since the set of noninteracting E-V-densities is dense in the set of interacting E-V-densities. The question whether these two sets are in fact identical is still an open question. We further discussed two systematic approaches for the construction of the exchange-correlation functional and potential.

What can we say about future developments within density functional theory? There have been many extensions of density functional theory involving spins, relativistic effects, temperature, superconductivity and time-dependent phenomena. The last few years we have, for instance, seen many applications of response properties, rather than ground state properties, using time-dependent density functional theory. For these extended density functional theories it is, of course, more difficult to provide a rigorous theoretical basis. This is, however, not particular to density functional theory, but applies to any method that deals with many-body systems, especially if one is interested in phenomena like superconductivity or interactions with laser fields. Nevertheless, also for these complicated cases simple density functionals have provided encouraging results although there is still a clear need for more accurate density functionals. In view of the success of density functional theory for ground state calculations it seems worthwhile to explore these new areas.

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